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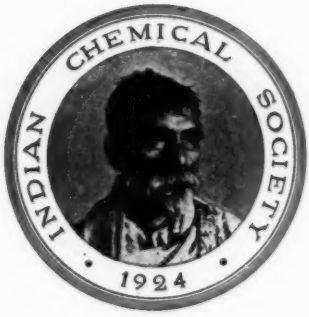

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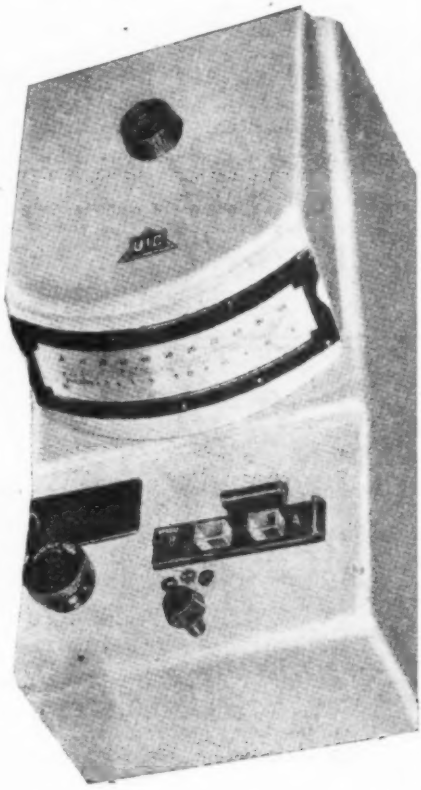

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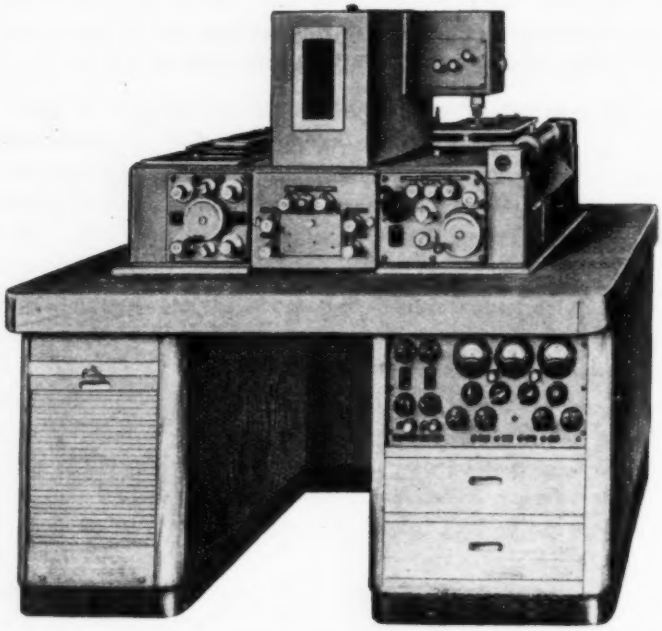

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DIELECTRIC CONSTANT AND DIPOLE MOMENT: CHROMONES, FLAVONES AND BENZYLIDENE-COUMARANONES

By S. K. K. Jatkar and C. M. Deshpande

The dielectric constants and densities of 2:6-dimethyl-γ-pyrone, 2-methyl-5-hydroxychromone and 2-methyl-7-methoxychromone, four flavones and two benzylidene-coumaranones have been measured at various concentrations and various temperatures. The dipole moments have been deduced by applying the new equation, and the values obtained have been compared with the values calculated theoretically.

The moment of 2:6-dimethyl-γ-pyrone in benzene solution was measured by Hunter and Partington (*J. Chem. Soc*, 1933, 87) and by Govinda Rao (*Proc. Ind. Acad Sci.*, 1936, **4A**, 687). In the present work the data of these authors have been recalculated by applying the new equation. The dielectric constants and densities of 2-methyl-5-hydroxychromone and 2-methyl-7-methoxychromone, 4′-methoxyflavone, 4′-methoxy-6-methylflavone, 4′-benzyloxyflavone, 6-benzoyl-4′-methoxyflavone, 4′-methoxy- and 4′-methoxy-5-methyl-benzylidene-coumaranones in benzene have been measured over a range of temperatures at various concentrations.

The moments of these compounds have been measured for the first time. The results are shown in the tables.

Experimental

Thiophene-free benzene was made as described previously (this *Journal*, 1960, **37**, 1). It was dried over anhydrous calcium chloride and forzen. The portion that froze at 5.5° was finally distilled over P_2O_5.

2-Methyl-5-hydroxychromone was recrystallised from alcohol till the observed m.p. agreed with the literature value. In the case of the rest of the compounds, the samples available were combustion samples and were used as such.

Table I

	Obs. M.P.	Lit. M.P.
2-Methyl-5-hydroxychromone	92°	92°
2-Methyl-7-methoxychromone	113°	113°
4′-Methoxyflavone	157°	157·58°
6-Methyl-4′-methoxyflavone	170°	170°
4′-Benzyloxyflavone	190°	190°
6-Benzoyl-4′-methoxyflavone	205°	205°
4′-Methoxybenzylidene-coumaranone	134°	133·53·4·5°
4′-Methoxy-5-methylbenzylidene-coumaranone	152°	152°

TABLE IIA*

2 : 6-*Dimethyl-γ-pyrone.*

Solvent : benzene. P_E = 144.0.

f_2.	ϵ_{12}.	d_{12}.	P_2.	μ_{new}.	ϵ_{12}.	d_{12}.	P_2.	μ_{new}.
	Temp. = 10°.				Temp. = 20°.			
0.00000	2.299	0.8884	...	...	2.280	0.8777	...	...
0.00531	2.469	0.8899	2976	3.82	2.442	0.8792	2863	3.81
0.01057	2.633	0.8913	2934	3.80	2 598	0.8307	2830	3 79
0.01108	2.640	0.8913	2852	3.75	2.605	0.8807	2762	3 76
0 01492	2.765	0.89224	2896	3.77	2 724	0.8319	2795	3.76
0.01967	2.908	0.8938	2882	3.76	2.862	0.8833	2780	3.75
	Temp. = 30°.				Temp. = 40°.			
0.00000	2 261	0.8669	...	...	2.242	0.8561	...	...
0 00531	2.415	0.8685	2656	3.73	2 387	0.8577	2656	3.79
0.01057	2.563	0.8701	2678	3.74	2 529	0 8596	2621	3.75
0.01108	2.570	0.8701	2626	3.70	2.535	0.8596	2572	3 72
0 01492	2.682	0.8713	2668	3.74	2 641	0.8608	2587	3 74
0.01967	2.816	0.8727	2669	3.74	2.770	0.8621	2598	3.74

μ_D : 10°−4.47 ; 20°−4.48 ; 30°−4.51 ; 40°−4.51.

* Govinda Rau, *loc. cit.*

TABLE IIB*

Solvent : benzene. μ_D = 4.05. Temp. = 25°.

f_2.	ϵ_{12}.	d_{12}.	P_2.	μ_{new}.
0.00000	2.277	0.8788	...	...
0.00871	2 502	0.8805	2445	3 51
0.00998	2.513	0.8809	2265	3.30
0.01512	2.666	0.8827	2440	3.50
0.01957	2.806	0.8850	2522	3.57

* Hunter and Partington, *loc. cit.*

TABLE III

**2-Methyl-5-hydroxychromone.*

Solvent : benzene. P_E = 188.1.

Temp.	ϵ_{12}.	d_{12}.	P_2.	μ_{new}.	ϵ_{12}.	d_{12}.	P_2.	μ_{new}.	ϵ_{12}.	d_{12}.	P_2.	μ_{new}.
		w_2 = 0.01347.				w_2 = 0.02218.				w_2 = 0.030167.		
20°	2.457	0.88265	2249	3.32	2.542	0.88529	2200	3.28	2.624	0.8869	2207	3.29
25°	2.447	0.87676	2261	3 36	2.535	0 87936	2216	3.32	2.617	0.88103	2230	3.35
30°	2.440	0.87076	2301	3.42	2 528	0.87338	2261	3.39	2.611	0.87502	2265	3.39
35°	2.433	0.86412	2354	3.49	2.520	0.86727	2279	3 43	2.603	0.86912	2282	3 43
40°	2.425	0.85783	2405	3.56	2.513	0.86144	2311	3.48	2.598	0.86276	2329	3.50
45°	2 416	0.85154	2418	3.60	2.503	0.85501	2311	3.52	2 592	0 85640	2370	3 56
50°	2 408	0.84525	2444	3 65	2.498	0.84888	2359	3 59	2.585	0.85004	2405	3 60

* Present work.

TABLE IV

*7-*Methoxy-2-methylchromone.*

Solvent: benzene. $P_E = 207.04$.

Temp.	ϵ_{12}.	d_{12}.	P_2.	μ_{new}.	ϵ_{12}.	d_{12}.	P_2.	μ_{new}.
		$w_2 = 0.007597$.				$w_2 = 0.009872$		
25°	2.358	0.8756	2604	3.61	2.381	0.8746	2601	3.61
30°	2.346	0.8696	2554	3.61	2.367	0.8686	2543	3.59
35°	2.333	0.8638	2528	3.61	2.356	0.8626	2524	3.61
40°	2.322	0.8576	2503	3.62	2.342	0.8564	2504	3.62
45°	2.309	0.8518	2478	3.63	2.329	0.8504	2466	3.62

* Present work.

TABLE V

*4′-*Methoxyflavone.*

Solvent: benzene. $P_E = 289.5$.

Temp.	ϵ_{12}.	d_{12}.	P_2.	μ_{new}.	ϵ_{12}.	d_{12}.	P_2.	μ_{new}.
		$w_2 = 0.01047$.				$w_2 = 0.009292$.		
25°	2.330	0.8762	1807	2.87	2.322	0.8754	1765	2.83
30°	2.317	0.8700	1759	2.85	2.309	0.8692	1738	2.83
35°	2.304	0.8638	1711	2.83	2.298	0.8630	1710	2.83
40°	2.292	0.8576	1711	2.85	2.285	0.8568	1683	2.82
45°	2.280	0.8514	1663	2.82	2.272	0.8506	1656	2.82

*Present work.

TABLE VI

*6-*Methyl-4′-methoxyflavone.*

Solvent: benzene. $P_E = 303.5$.

Temp.	ϵ_{12}.	d_{12}.	P_2.	μ_{new}.	ϵ_{12}.	d_{12}.	P_2.	μ_{new}.
		$w_2 = 0.0044303$.					$w_2 = 0.0072417$.	
20°	2.336	0.87882	1744	2.78	2.351	0.88029	1765	2.80
25°	2.327	0.87134	1744	2.80	2.342	0.87466	1729	2.79
30°	2.317	0.86721	1684	2.76	2.332	0.86383	1692	2.77
35°	2.308	0.86102	1684	2.79	2.322	0.86263	1655	2.76
40°	2.298	0.85483	1624	2.75	2.311	0.85643	1618	2.74
45°	2.288	0.84864	1624	2.77	2.301	0.85023	1581	2.72
50°	2.278	0.87245	1563	2.73	2.290	0.84403	1545	2.71

* Present work.

TABLE VII

*4′-*Benzyloxyflavone.*

Solvent: benzene. $w_2 = 0.006395$. $P_E = 381.4$.

Temp.	ϵ_{12}.	d_{12}.	P_2.	μ_{new}.
25°	2.335	0.8772	3697	4.25
30°	2.321	0.8708	3646	4.25
35°	2.310	0.8646	3594	4.25
40°	2.297	0.8584	3491	4.21
45°	2.283	0.8520	3441	4.21

* Present work.

TABLE VIII

*6-*Benzoyl-4′-methoxyflavone.*

Solvent: benzene. $w_2 = 0.006726$. $P_E = 406.8$.

Temp.	ϵ_{12}.	d_{12}.	P_2.	μ_{new}.
25°	2.315	0.8760	2755	3.57
30°	2.302	0.8702	2702	3.56
35°	2.291	0.8644	2650	3.55
40°	2.280	0.8586	2696	3.54
45°	2.269	0.8527	2543	3.52

* Present work.

TABLE IX

4′-Methoxybenzylidene-coumaranone.
Solvent: benzene. $P_E = 284.9$.

Temp.	ϵ_{12}.	d_{12}.	P_2.	μ_{new}.	ϵ_{12}.	d_{12}.	P_2.	$\bar{\mu}_{new}$.	ϵ_{12}.	d_{12}.	P_2.	μ_{new}
		$w_2 = 0.01495$.				$w_2 = 0.01910$				$w_2 = 0.02609$.		
25°	2.348	0.8784	1670	2 75	2.371	0 8794	1690	2.76	2 407	0.8814	1692	2 77
30°	2.336	0.8730	1637	2.73	2.359	0 8738	1678	2.72	2.393	0.8758	1673	2.77
35°	2.325	0.8674	1620	2.74	2.346	0.8682	1625	2.75	2.378	0.8702	1625	2.75
40°	2.314	0.8622	1586	2.73	2.333	0.8630	1590	2.74	2.365	0 8648	1586	2 73
45°	2.303	0.8568	1570	2.73	2.321	0 8576	1559	2.71	2.353	0.8594	1576	2 74

* Present work.

TABLE X

4′-Methoxy-5-methylbenzylidene-coumaranone.
Solvent: benzene. $P_E = 303.5$.

Temp.	ϵ_{12}.	d_{12}.	P_2.	μ_{new}.	ϵ_{12}.	d_{12}.	P_2.	$\bar{\mu}_{new}$.
		$w_2 = 0.007415$.				$w_2 = 0.008405$.		
25°	2.311	0.8760	1724	2 78	2.316	0.8766	1711	2 77
30°	2.298	0.8702	1689	2.77	2.304	0.8708	1679	2.76
35°	2.287	0.8642	1652	2.73	2.292	0 8648	1647	2.75
40°	2.276	0.8582	1616	2.74	2.281	0.8588	1615	2.74
45°	2.263	0.8522	1581	2.72	2.268	0.8528	1584	2 73

* Present work.

TABLE XI

Moments.

Compound.	Solvent.	μ_{new} / $1kT$.	μ_{new} / $1.5kT$.	$\mu_{calc.}$	μ_D.
2 : 6-Dimethyl-γ-pyrone	Benzene*	3.78		2.16 I	4.49
	Benzene†	3.53			4.05
2-Methyl-5-hydroxychromone	Benzene**	3.32		3 25 I	
		3.60		5.12 II	
		(4.2)		4.18	
2-Methyl-7-methoxychromone	Benzene**	3.61		3.85	
4′-Methoxyflavone	Benzene**	2.83	3 47	3.30	
6-Methyl-4′-methoxyflavone	Benzene**	2.84	3.48	3.30	
4′Benzyloxyflavone	Benzene**			3.30 II	
		4.24		6.2 III	
6-Benzoyl-4′-methoxyflavone	Benzene**	3.58		3.92	
4′-Methoxybenzylidene-coumaranone	Benzene**	2.75		2.90	
4′-Methoxy-5-methylbenzylidene-coumaranone	Benzene**	2 75		2.90	

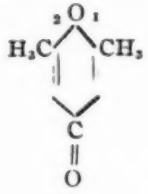
* Govinda Rao, *loc. cit.*
† Hunter and Partington, *loc. cit.*
** Present work.

DISCUSSION

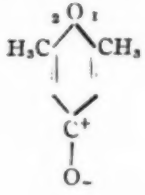
2:6-*Dimethyl-γ-pyrone*

The data of Hunter and Partington (*loc. cit.*) and of Govinda Rao (*loc. cit.*) have been recalculated by applying the new equation. The value of the former authors is lower than that given by the latter. The moment obtained from the recalculation of the data of Govinda Rao is 3.78 and is independent of temperature and concentration.

In addition to the normal quinonoid structure (I) for γ pyrone, Berson (*J. Amer. Chem. Soc.*, 1953, **75**, 3521) has indicated a number of dipolar structures for γ-pyrone. Thus, the compound, dimethyl-γ-pyrone, will have the following structures.



(I)



(II)

Each of the C—O bond will be reduced to a moment of 0.74 because of mutual induction. The resultant of the two is 0.74.

Structure (I): The resultant 0.74 of C—O (1) and C—O (2) acts in opposite direction to the moment 2.90 of C=O bond and gives a resultant molecular moment of 2.16.

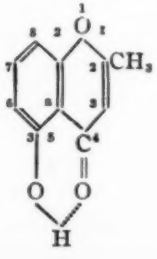
Structure (II): The full moment of C=O is 5.80. This together with the resultant moment of C—O (1) and C—O(2) gives the molecular moment, the value of which is 5.06.

The mean of the two values is 3.61, which compares favourably with the observed value of 3.78, obtained by the new equation.

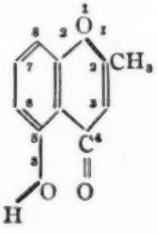
It seems that the ionic character of C=O bond in this compound is increased to 75% instead of the normal value of 50%.

2-*Methyl-5-hydroxychromone*

The moment of 2-methyl-5-hydroxychromone in benzene solution has been measured for the first time. The new moment of this compound is independent of concentration, but varies with temperature.



(I)



(II)

C—O (1) is reduced to a value of 0.74 because of induction from C—O (2), the effect of induction from C—O (3) being negligible. C—O (2) is reduced to a moment of 0.555 because of induction from C—O (1) and C—O (3). C—O (3) is reduced to a value of 1.295 because of induction from C—O (2), the effect of induction from C—O (1) being very small. C=O and O—H remain unaffected, and have the moment values of 2.90 and 2.40 respectively.

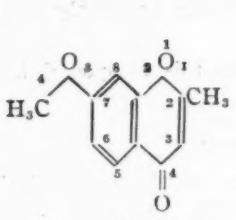
Structure (I): The moment along C_5-C_6 is 3.14 (0.74 + 2.40) and that along C—O (3) is 4.195 (1.295 + 2.90). The resultant of these two is 3.78. This resultant together with the moment 0.555 along C_5-C_6 will give the molecular moment, the value of which is 3.25.

Structure (II): The moment along C_5-C_6 is 0.555 and that along C—O (3) is 4.195. The resultant of these two is 3.947. This resultant together with the moment of 1.66 along C_5-C_6(2.4-0.74) gives the molecular moment, the value of which is 5.12.

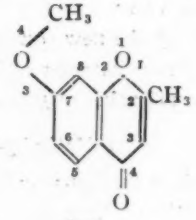
The observed moment of the compound varies with temperature, the va'ue being 3.32 to 3.60. It seems that with increase of temperature, the hydrogen bond breaks up and the contribution due to structure (II) becomes more and more. The moment increases with temperature and asymptotically reaches a value of 4.2 at a higher temperature. This value compares with the mean of the two values for structure (I) and structure (II).

2-Methyl-7-methoxychromone

The moment of 2-methyl-7-methoxychromone in benzene has been measured for the first time. The new moment is 3.61, which is independent of temperature and concentration. The moment can be theoretically calculated for this compound. The two possible structures for this compound are shown below.



(I)



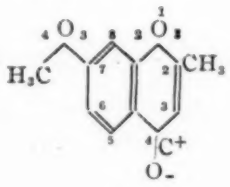
(II)

C—O (1) and C—O (2) are each reduced to 0.74 because of induction. C—O(3) and C—O (4) are each reduced to 0.99 because of induction. The effect of induction of C—O (1) and C—O (2) on C—O (3) and C—O (4) and *vice versa* is very very small. The moment of C=O is 2.90.

Structure (I): The resultant 0.74 of C—O (1) and C—O (2) adds on to the resultant 1.14 of C—O (3) and C—O (4) and gives a moment of 1.88. This together with the moment 2.9 of C=O gives the molecular moment, the value of which is 1.02.

Structure (II): The resultant of C—O (1) and C—O (2) acts in a direction opposite to the resultant of C—O (3) and C—O (4) and gives a resultant moment of 0.40 in the direction of C=O. The net molecular moment is 3.30.

In addition to these two structures, there may be a third dipolar structure as in the case of 2 :6-dimethyl-γ-pyrone.



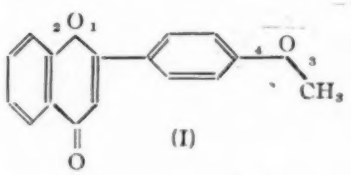
(III)

Structure (III) : The full moment of C=O is 5.8. The resultant of C—O (1) and C—O (2) combines with the resultant of C—O (3) and C—O (4), and gives a moment value of 1.88. This together with the full moment of C=O bond affords the molecular moment, the value of which is 3.92.

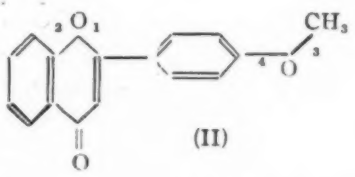
It appears that only structures (II) and (III) contribute to the molecular moment. The mean of the values for these two structures is 3.61, which compares with the observed value of 3.61. It appears that in this compound, as in the case of 2 :6-dimethyl-γ-pyrone, the ionic character of C=O bond has increased to 75% instead of the normal value of 50%. The results are summarised in Table XI.

4′-Methoxyflavone

The moment of 4′-methoxyflavone in benzene solution is 2.83, as obtained by the new equation. The moment has been measured for the first time and is independent of temperature and concentration. The compound can have two possible structures, structure (I) and structure (II).



(I)



(II)

C—O (1) and C—O (2) are each reduced to a moment of 0.74 because of mutual induction. Similarly C—O (3) and C—O (4) are each reduced to a value of 0.99 due to mutual induction. The effect of induction of C—O (1) and C—O (2) on C—O (3) and C—O (4) and *vice versa* is negligible.

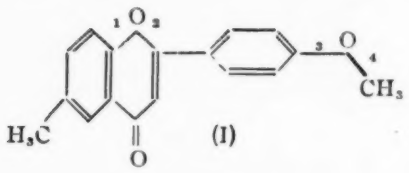
Structure (I) : The resultant of C—O (1) and C—O (2) is 0.74. The resultant of C—O (3) and C—O (4) is 1.14. These two, being parallel, add on and give a moment value of 1.88. This, together with the moment of 2.90 of C=O, gives 1.02 as the value of the molecular moment.

Structure (II) : The resultant of 0.74 of C—O (1) and C—O (2) is parallel to and in opposite direction of the resultant 1.14 of C—O (3) and C—O (4). The net resultant is 0.40 in the direction of C=O. The molecular moment is thus 3.30.

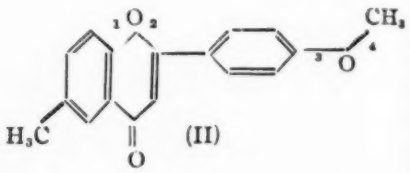
The observed moment of 2.83 may be increased to a value of 3.47 by increasing $2j+1=2$ $(1kT)$ to $2j+1=3$ $(1.5kT)$. This value compares with the value calculated for structure (II).

6-Methyl-4′-methoxyflavone

The new moment of 6-methyl-4′-methoxyflavone in benzene is 2.76, which is independent of temperature and concentration. The moment has been measured for the first time.



(I)

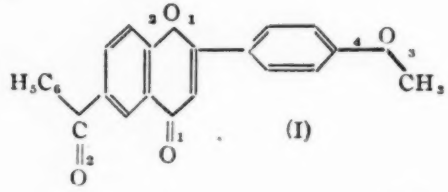


(II)

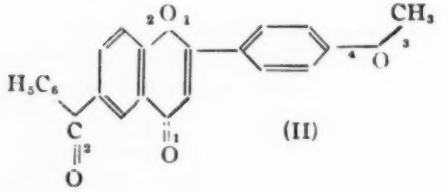
6-Methyl 4′-methoxyflavone has two structures similar to those of 4′-methoxyflavone. The moment for structure (I) is 1.02 and that for structure (II) is 3.30. The observed moment of 2.84 can be increased to a value of 3.48 by increasing $2j+1=2$ $(1kT)$ to $2j+1=3$ $(1.5kT)$. This compares with the value calculated for structure (II).

6-Benzoyl-4′-methoxyflavone

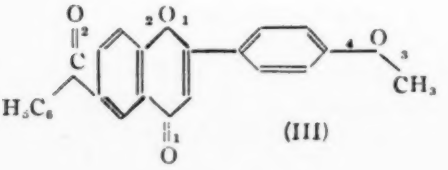
The moment of 6-benzoyl-4′-methoxyflavone, as obtained by the new equation, is 3.55, which is independent of temperature. The moment of this compound has been determined for the first time.



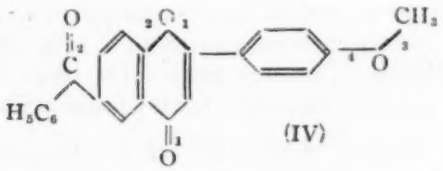
(I)



(II)



(III)



(IV)

C—O (1) and C—O (2) are each reduced to a moment of 0.74, and C—O (3) and C—O (4) are each reduced to a moment of 0.99 because of mutual induction. The effect of induction due to C—O (1) and C—O (2) on C—O (3) and C—O (4) and *vice versa* is negligible. The bonds C=O (1) and C=O (2) are also unaffected, as the induction is very small.

Structure (I): The resultant 0.74 of C—O (1) and C—O (2) and 1.14 of C—O (3) and C—O (4) add on to give a moment of 1.88. The resultant of C=O (1) and C=O (2) is 5.80. The resultant of the two is the molecular moment, the value of which is 3 92.

Structure (II): The resultant of C—O (1) and C—O (2) and of C—O (3) and C—O (4) oppose each other and give a moment value of 0.4. This together with the resultant 5 8 of C=O (1) and C=O (2) affords a value of 6.20, which is the value of the molecular moment.

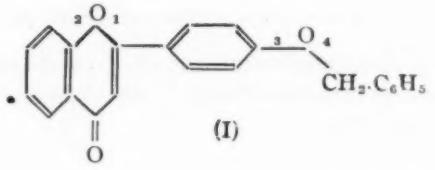
Structure (III): The moment of C=O (1) cancels that of C=O (2). The resultant 0.74 of C—O (1) and C—O (2) adds on with the resultant 1.14 of C—O (3) and C—O (4) and provides the value of 1.88, which is the molecular moment.

Structure (IV): C=O (1) cancels C=O (2). The resultant of C—O (1) and C—O (2) opposes the resultant of C—O (3) and C—O (4) and gives 0.4 as the value of the molecular moment.

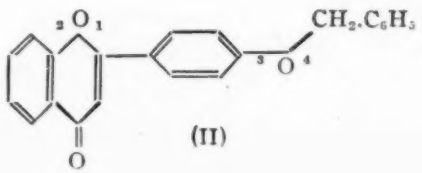
The observed moment of 3.55 indicates that structure (I) predominates with little contribution from structures (III) and (IV).

4′-Benzyloxyflavone

The new moment of 4′-benzyloxyflavone in benzene is 4.23, which is independent of temperature. The moment has been determined for the first time.



(I)



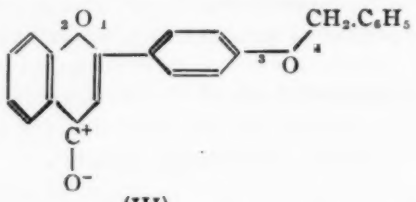
(II)

C—O (1) and C—O (2) are each reduced to a moment of 0.74 because of induction. Similarly, C—O (3) and C—O (4) are each reduced to a value of 0.99 due to induction. The effect of induction of C—O (3) and C—O (4) on C—O (1) and C—O (2) and *vice versa* is very small, and so is neglected. C=O remains unaffected.

Structure (I) : The resultant of C—O (1) and C—O (2) is 0.74. The resultant of C—O (3) and C—O (4) is 1.14. The two are parallel and in the same direction and so give a net moment of 1.88. This together with the moment of 2.90 of C=O affords a moment value of 1.02, which is the molecular moment.

Structure (II) : The resultant 0.74 of C—O (1) and C—O (2) opposes the resultant 1.14 of C—O (3) and C—O (4) and provides a resultant of 0.40 in the direction of C=O. The molecular moment is obtained by the addition of 0.40 with the moment of 2.90 of the C=O bond. The molecular moment is 3.30.

In addition to the above two structures, 4′-benzyloxyflavone may have a structure of the type (III) similar to one suggested by Berson (*loc. cit.*) for dimethyl-γ-pyrone.



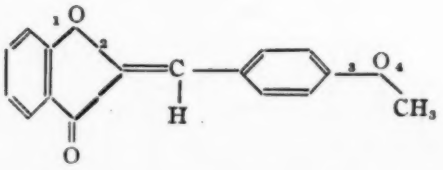
(III)

The resultant of C—O (1) and C—O (2) opposes the resultant of C—O (3) and C—O (4) and gives a net moment of 0.40 in the direction of C—O⁻. The resultant moment is 6.20 (5.8 + 0.4).

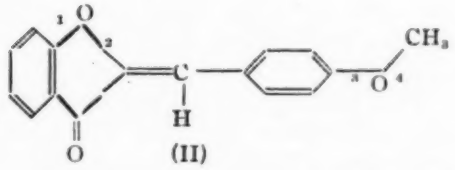
The observed moment of 4.23 indicates that structures (II) and (III) predominate with no contribution from structure (I). It appears that structure (III) contributes to the molecular moment to a large extent, nearly 50%, indicating that the ionic character of C=O bond in this compound is increased to about 75%. The results are summarised in Table XI.

4′-Methoxybenzylidene-coumaranone

The new moment of 4′-methoxybenzylidene-coumaranone in benzene is 2.76, which is independent of temperature and concentration. The moment of this compound has been determined for the first time.



(I)



(II)

C—O (1) and C—O (2) are each reduced to a moment value of 0.99 and C—O (3) and C—O (4) to a value of 0.99 because of mutual induction. The induction of C—O (1) and C—O (2) on C—O (3) and C—O (4) and *vice versa* is negligible.

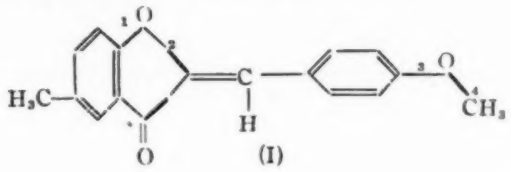
Structure (I) : The moment of C—O (1) and C—O (2) is 1.14 and that of C—O (3) and C—O (4) is 1.14. The two are parallel and in the same direction and so add up to give a moment of 2.28. This together with the moment 2.9 of C=O gives the molecular moment, the value of which is 0.62.

Structure (II) : The resultant 1.14 of C—O (1) and C—O (2) and 1.14 of C—O (3) and C—O (4) are parallel but in opposite direction. The resultant of the two is zero. This together with the moment 2.9 of C=O gives 2.9 as the value for the molecular moment.

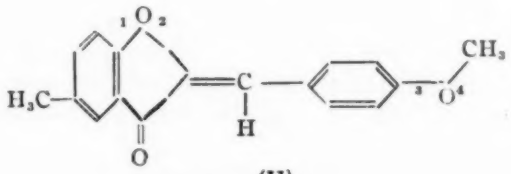
The observed moment of 2.75 indicates that the molecular moment is entirely due to structure (II) with a small contribution from structure (I).

4′-Methoxy-5-methylbenzylidene-coumaranone

The moment of 4′-methoxy-5-methylbenzylidene-coumaranone in benzene has been measured for the first time. The moment obtained by the new equation is 2.75, which is independent of temperature and concentration. The compound has two structures, similar to those of 4′-methoxybenzylidene-coumaranone.



(I)



(II)

The moment calculated for structure (I) is 0.62 and that for structure (II) is 2.90. The observed value of 2.75 shows that structure (II) predominates with very little contribution from structure (I).

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STUDIES ON THE NATURE OF RACEMIC MODIFICATIONS OF OPTICALLY ACTIVE COMPOUNDS IN THE SOLID STATE. PART XVIII. CAMPHANOQUINOXALINE, CAMPHANODIHYDROQUINOXALINE, *m*- AND *p*-PHENYLENE-*bis*-IMINO- AND -AMINOCAMPHORS

By Bawa Kartar Singh and Bhupendra Sahai Saxena

The racemic forms of camphanoquinoxaline, *m*-phenylene-*bis*-imino- and -aminocamphors occur as recemates (*dl*), whereas those of camphanodihydroquinoxaline and *p*-phenylene-*bis*-iminocamphor exist as solid solutions. The stability of these racemic forms has been discussed with the aid of their melting point—composition diagrams.

In this communication we have discussed the nature of racemic modifications of camphanoquinoxaline, camphanodihydroquinoxaline, *m*- and *p*-phenylene-*bis*-imino- and -aminocamphors.

By the application of Roozeboom's phase rule method of the melting point-composition diagrams to the mixtures of racemic and *dextro* forms of these substances, the racemic forms have been diagnosed as true *dl* compounds or *solid solutions* according as these diagrams consist of three curves or a single curve. No example of the racemic form occurring as *mixture*, providing two curves in the melting point—composition diagrams, has been found in the present study.

Excepting the *p*-phenylene-*bis*-imino- and -amino-*dl*-camphors, all the other racemic forms described herein are new substances.

Experimental

Camphanoquinoxalines were prepared both by the method of Singh and Mazumder (*J. Chem. Soc.*, 1919, **115**, 566) and also by heating the equimolecular mixture of *o*-phenylenediamine and camphorquinone in dry state with an excess of anhydrous sodium sulphate on a water-bath for an hour, the latter method affording the better yield.

For the preparation of camphanodihydroquinoxaline from the corresponding camphanoquinoxaline, reduction of the ethereal solution of the latter with zinc dust and 10% KOH was found to be more satisfactory than the Sn-HCl method used by Singh *et al.* (*ibid.*, 1920, **117**, 980). The melting points of *d*-camphanoquinoxaline and its reduction product, *d*-camphanodihydroquinoxaline, are found to agree with those reported earlier (*loc. cit.*), but the rotatory power of *d*-camphanodihydroquinoxaline is found to be much higher, $[\alpha]_D^{35}$ in chloroform, $-212°.5$ (reported $-175°$).

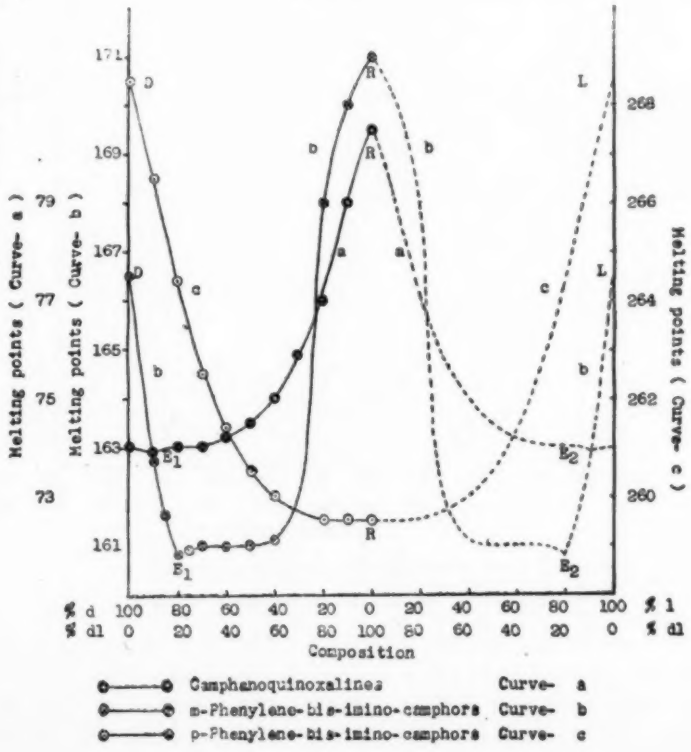
m-Phenylene-*bis*-iminocamphor (Singh and Mazumder, *loc. cit.*), *p*-phenylene-*bis*-imino- and -aminocamphors (Singh and Bhaduri, this *Journal*, 1930, 7, 545) were prepared according to methods described. The melting points of the *dextro* isomers of *m*-phenylene-*bis* imino- and -aminocamphors (Table I) differ considerably from those reported earlier (150-51° and 163° respectively). The rotatory powers of these compounds are, however, in good agreement with the reported values.

Known proportions of *dextro* and racemic forms were powdered intimately in an agate mortar and the melting point of each composition was determined as the mean of six readings taken with a Siebert and Kühn thermometer, graduated in 0.1°. The experimental results are represented in the form of curves (Figs. 1 and 2) in which the melting points are plotted against composition.

Discussion

Camphanoquinoxaline (Fig. 1, a).—This diagram consists of three curves DE_1, E_1RE_2 and E_2L, which shows that the racemic form is a true *dl* compound. The range of existence of the racemic form is great which is indicated by the central portion of the diagram occupying a large area, almost the whole of the diagram.

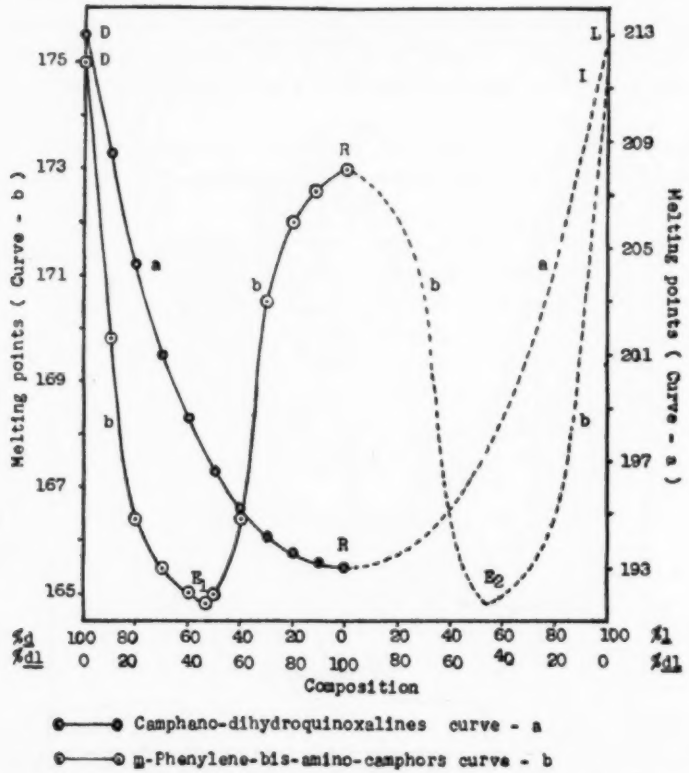
Fig. 1



m-*Phenylene*-bis-*iminocamphor* (Fig. 1, b).—In this case also the diagram consists of three curves and the racemic form is shown to be a true *dl* compound. It has a fair range of existence. No appreciable dissociation of the racemic form into its optically active components is shown as the central portion of the diagram is steep. The horizontal portion of the curve *dl-d* between the composition range 30 *dl* : 70 *d* to 50 *dl* : 50 *d* shows that the racemic form affords a solid solution with the active form in this region.

p-*Phenylene*-bis-*iminocamphor* (Fig. 1, c) *and Camphanodihydroquinoxaline* (Fig. 2, a).—Each of these diagrams consists of a single continuous curve without any *singular* point on it and is concave to the composition axis. The racemic forms of each of these compounds are therefore *solid solutions* of equimolecular quantities of the *dextro* and *laevo* forms.

FIG. 2



m-*Phenylene*-bis-*aminocamphor* (Fig. 2, b).—This also shows the typical characteristics of the racemic form, being a true *dl* compound. The eutectic points, E_1 and E_2, are sharp and well defined. The central portion is somewhat rounded which shows that the racemic form partially dissociates into its component active forms at its melting point.

TABLE I

Physical properties and chemical analyses of compounds.

No.	Compounds.		M.P.	Colour and cryst. form.	% Nitrogen. Found.	Calc.	Remarks.
1.	Camphanoquinoxalines	*d-*	74.0°	Colorless thin rectangular plates	12.02	11.76	Highly soluble in all the organic solvents. Insoluble in water.
	$C_{16}H_{18}N_2$	*dl-*	80.5°	,, prismatic needles	11.98		
2.	*m*-Phenylene-*bis*-iminocamphors	*d-*	166.5°	Yellow prismatic needles	7.15	6.93	Highly soluble in chloroform, benzene, acetone; less so in methyl alcohol. ethyl alcohol and ethyl acetate; insoluble in water.
	$C_{26}H_{32}O_2N_2$	*dl-*	171.0°	Do	7.22		
3.	*p*-Phenylene-*bis*-iminocamphors	*d-*	268.5°	Golden yellow spindles	7.16	6.93	
	$C_{26}H_{32}O_2N_2$	*dl-*	259.5°	,, ,, thin rectangular plates	7.18		
4.	Camphanodihydroquinoxaline	*d-*	213.0°	Colorless long silky needles	11.91	11.67	Highly soluble in chloroform, benzene, acetone, ethyl acetate; less so in methyl alcohol and ethyl alcohol; insoluble in water.
	$C_{16}H_{20}N_2$	*dl-*	193.0°	,, fine ,, ,,	11.94		
5.	*m*-Phenylene-*bis*-aminocamphors	*d-*	175.0°	,, prismatic ,,	7.13	6.86	
	$C_{26}H_{36}O_2N_2$	*dl-*	173.0°	,, silky leaflets	7.12		
6.	*p*-Phenylene-*bis*-aminocamphors	*d-*	208.0°	,, prismatic needles	7.14	6.86	
	$C_{26}H_{36}O_2N_2$	*dl-*	210.2°	,, Do	7.14		

p-*Phenylene*-bis-*aminocamphor*.—The different mixtures of the *dextro* and racemic modifications of this substance do not have any definite and sharp melting points. It is therefore not possible to draw any conclusion about the nature of its racemic form.

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REDUCTION OF ACID POTASSIUM PERMANGANATE BY IODIDE, NITRITE AND BROMIDE

By B. P. Gyani and S. N. Prasad

Acid potassium permanganate may be quantitatively reduced to Mn^{2+} by iodide or nitrite when conditions are suitable ($N/10$ to $5N$-H_2SO_4); 5.0 and 2.5 moles of KI and KNO_2 respectively are required per mole of $KMnO_4$. On the other hand, reduction by KBr ($N/10$ to $2N$-H_2SO_4) stops short at the MnO_2 stage. The complete reduction to Mn^{2+} may perhaps be attained at 2 to $3N$-H_2SO_4, but further increase in acid concentration (up to $8N$) leads to evolution of oxygen and the consumption of KBr again drops steadily. In the KI titration of $KMnO_4$, there is an initial inflection at 0.5 mole KI, and in the KNO_2 titration, at 1.5 moles, but each of these shifts to larger amounts as the sulphuric acid concentration in the mixture is increased.

This work is in continuation of previous ones concerning oxidising properties of potassium dichromate, potassium iodate and other familiar oxidising agents (this *Journal*, 1954, **31**, 561; 1955, **32**, 313; 1956, **33**, 871; 1957, **34**, 252; 1958, **35**, 721). Although most of the potentiometric titrations described in these papers are familiar, the conditions of their satisfactory operation are not known in detail. It has been shown that in many of these titrations, the quantitative result may be completely upset if, for example, the acid concentration is not properly fixed. The same has again been observed with the permanganate titrations, which are described below.

Incidentally, we find that although the reduction of iodate by iodide or bromide, studied by Britton *et al.* (*J. Chem. Soc.*, 1952, 3877 et seq), leads to similar results, the reduction of $KMnO_4$ by the same agents leads to quite different results.

The gradual reduction of $KMnO_4$ may take place in many ways. The main steps may be written down as follows:

$$2\,MnO_4^- \rightleftharpoons MnO_4^{3-} + MnO_2 + 2\,O \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

$$2\,MnO_4^- + 2H^+ \rightleftharpoons 2MnO_2 + H_2O + 3\,O \quad \ldots \quad \ldots \quad (2)$$

$$2\,MnO_4^- + 8H^+ \rightleftharpoons 2Mn^{3+} + 4H_2O + 4\,O \quad \ldots \quad \ldots \quad (3)$$

$$2\,MnO_4^- + 6H^+ \rightleftharpoons 2Mn^{2+} + 3H_2O + 5\,O \quad \ldots \quad \ldots \quad (4)$$

Thus, in a titration with KI, for example, if all these reductions can be realised, one may expect inflections at 2, 3, 4 and 5 moles KI per mole $KMnO_4$. Many additional inflections are possible, e.g., if the available oxygen oxidises KI to KIO_3.

$$2\,MnO_4^- + KI + 2H^+ \rightleftharpoons H_2O + 2MnO_2 + KIO_3 \quad \ldots \quad (5)$$

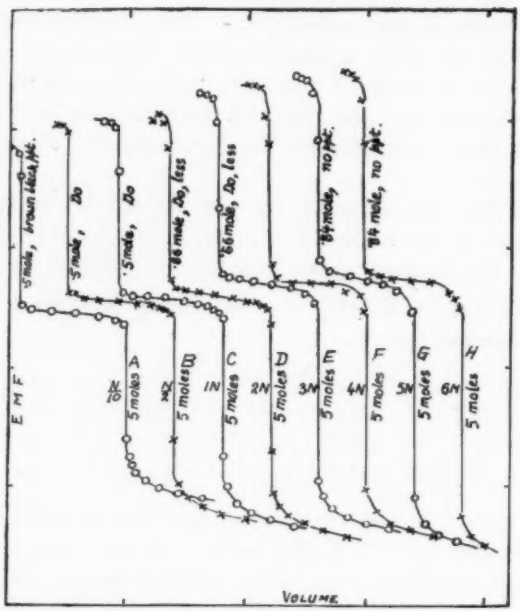
Experimental

The experimental procedure has been fully described in a previous paper (*loc. cit.*, 1954). Generally 100 c.c. of $M/200$-$KMnO_4$ was taken in a titration vessel and the solution contained the desired amount of acid (H_2SO_4 or HCl). A bright

platinum foil electrode was used. $N/1$ solutions of KI, and $N/2$ solutions of KBr and KNO_3 were used for titration. Sufficient time was allowed for equilibrium to attain. No titration was completed in less than six hours.

Reduction by Iodide.—This reduction has been studied potentiometrically, perhaps, since 1921 by a number of workers. Hendrixon (*J. Amer. Chem. Soc.*, 1921, **43**, 14) detected only the final stage corresponding to reaction (4), *i. e.*, 5 moles KI per mole $KMnO_4$ ($H_2SO_4 \sim 1N$). Kolthoff (*Rec. trav. chim.*, 1921, **40**, 552) used low concentrations of H_2SO_4 (0.2 to 0.5N) and was again able to detect only the final inflection. Müller and Möllering (*Z. anorg. Chem.*, 1924, **141**, 111) used 0.1N-H_2SO_4 and HCl solutions and were able to detect both reactions (4) and (5), the latter corresponding to half mole KI. These workers left the questions open whether other reductions could be detected in these titrations, and whether there were indefinite shifts in the locations of inflections observed. To investigate these matters the titrations were carried out in the following sulphuric acid media: (A) $N/10$, (B) $N/2$, (C) $N/1$, (D) $2N$, (E) $3N$, (F) $4N$, G; $5N$ and (H) $6N$. The corresponding titration graphs are shown in Fig. 1.

FIG. 1

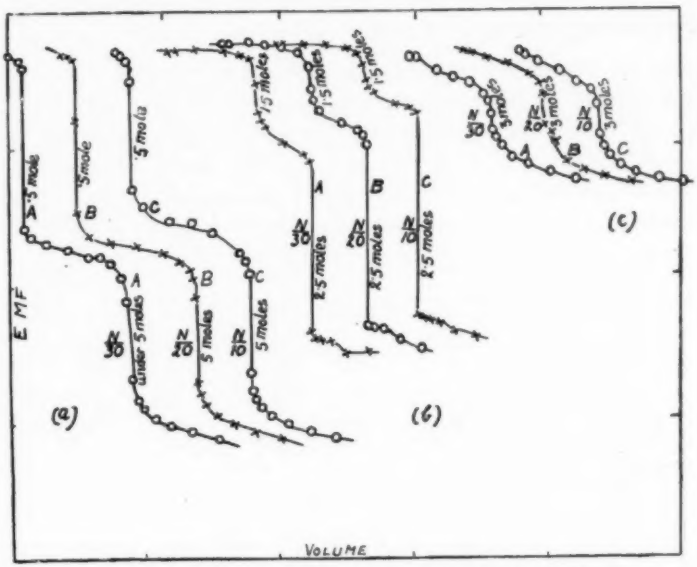


Titration of $M/200$-$KMnO_4$ (100 c c.) with N-KI in H_2SO_4 mixtures.

There are two inflections. The first is at first steady at half mole KI ($N/10$ to $N/1$-H_2SO_4), but at higher concentrations of acid it shows an increasing consumption of KI (0.66 mole at 2-3 N and 0.83 mole at 5-6 N). A dark brown precipitate appears with the first drop and increases during the titration, disappearing at the second inflection.

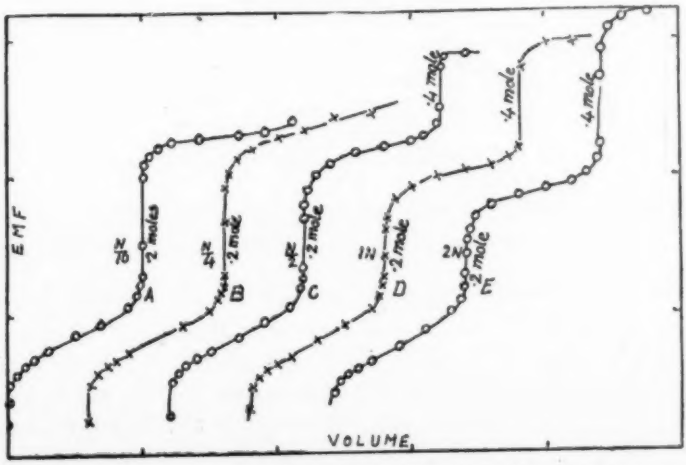
Fig. 2(*a*) shows the results when HCl replaces H_2SO_4 in the mixture, (A) $N/30$, (B) $N/20$, (C) $N/10$. The titration is not possible beyond $N/10$-HCl, as a perceptible odour of chlorine appears at that stage. The first inflection remains steady at half mole KI. The second inflection is at somewhat less than 5 moles and a little of the dark brown precipitate remains undissolved.

FIG. 2



(*a*). Titration of $KMnO_4$ with KI in HCl mixtures.
(*b*). $KMnO_4$ with KNO_2 in HCl mixtures.
(*c*). $KMnO_4$ with KBr in H_2SO_4 mixtures.

FIG. 3

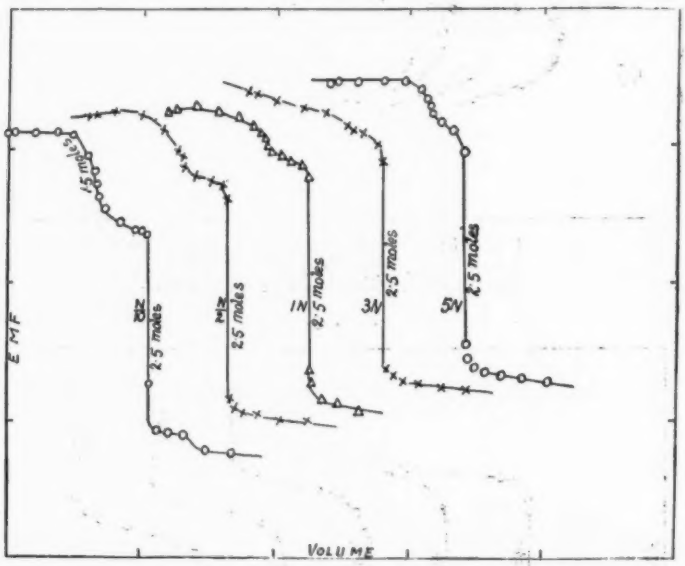


Titration of 100 c.c. of $M/40$-KI with $M/10$-$KMnO_4$ in HCl mixtures.

Fig. 3 shows the results obtained when these titrations were reversed. $M/40$-KI (100 c.c.) was taken in the cell and titrated with $M/10$ permanganate, acidified with HCl; (A) $N/10$, (B) $N/4$, (C) $N/2$, (D) $N/1$ and (E) $2N$. Since the permanganate delivered is preferentially consumed by KI, titration in $2N$-HCl now becomes possible. When the acid is less than $N/2$, there is only one inflection at 0.2 mole $KMnO_4$ per mole KI. At higher concentrations of HCl, there is another inflection at 0.4 mole. Iodine precipitates out in the beginning, but dissolves towards the second inflection, disappearing completely at 0.4 mole $KMnO_4$.

Reduction by Nitrite.—The solutions used were $M/200$-$KMnO_4$ (100 c.c. in the cell) and $0.463M$-KNO_2. The permanganate was acidified with HCl: (A) $N/30$, (B) $N/20$ and (C) $N/10$. The corresponding graphs are shown in Fig. 2(*b*). There are again two inflections as with KI, but the first one is at 1.5 moles, and the second at 2.5 moles KNO_2. Fig. 4 shows the results in H_2SO_4 mixtures. The notable feature is that the first inflection at 1.5 moles KNO_2 shifts to higher values, when acid concentration is increased (1.8 at $5N$-H_2SO_4).

FIG. 4

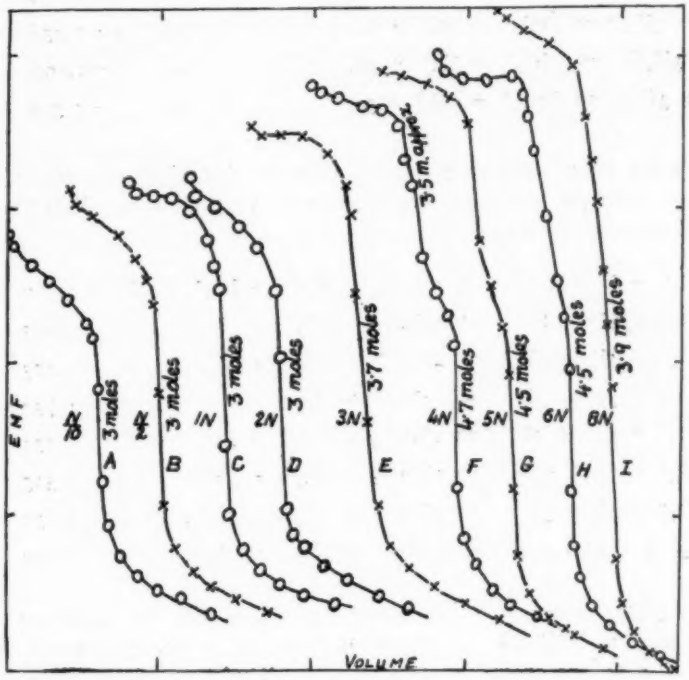


Titration of 100 c. c. of $M/200$-$KMnO_4$ with $0.463M$-KNO_2 in H_2SO_4 mixtures.

Reduction by Bromide.—$M/2$-KBr was used (delivered from burette). The permanganate was acidified on the one hand with H_2SO_4 and on the other, with HCl: (A) $N/30$, (B) $N/20$, (C) $N/1$, (D) $2N$, (E) $3N$, (F) $4N$, (G) $5N$, (H) $6N$ and (I) $8N$. The graphs for sulphuric acid mixtures appear in Fig. 5 and those for HCl mixtures in Fig. 2(*c*). In weaker acid solutions up to $2N$, there is a single inflection at 3.0 moles KBr. At $3N$-H_2SO_4 the inflection appears at 3.7 moles which increases

to 4.7 moles at 4*N* and thereafter decreases again (3.9 moles at 8*N*). Perhaps at an acid concentration, somewhere between 3*N*- and 4*N*-H_2SO_4, one may obtain a full reduction (inflection at 5.0 moles KBr). A special feature of titration with bromide is that some oxygen is evolved towards the end in strong H_2SO_4 solutions. The inflection remained steady at 3.0 moles in all the HCl solutions.

FIG. 5



Titration of 100 c.c. of *M*/200-$KMnO_4$ with *N*/2-KBr in H_2SO_4 mixtures.

DISCUSSION

When $KMnO_4$ is reduced, the E_o is positive at all stages of reduction and, hence, the reduction is always spontaneous.

$$MnO_4^- + e \rightleftharpoons MnO_4^{2-}, \quad \ldots \quad E_o = 0.54 \quad \ldots \quad (6)$$

$$MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 + 2H_2O, \quad \ldots \quad 1.59 \quad \ldots \quad (7)$$

$$MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{2+} + 2H_2O, \quad \ldots \quad 1.51 \quad \ldots \quad (8)$$

$$MnO_2 + 4H^+ + e \rightleftharpoons Mn^{3+} + 2H_2O, \quad \ldots \quad 0.97 \quad \ldots \quad (9)$$

$$Mn^{3+} + e \rightleftharpoons Mn^{2+}, \quad \ldots \quad 1.56 \quad \ldots \quad (10)$$

Some of the possible oxidations in the foregoing titrations are :

$$2I^- \rightleftharpoons I_2 + 2e, \qquad E_o = -0.337 \quad \ldots \quad (11)$$

$$HNO_2 + H_2O \rightleftharpoons NO_3^- + 3H^+ + 2e, \quad \ldots \quad -0.940 \quad \ldots \quad (12)$$

$$2Br \rightleftharpoons Br_2\,(liq) + 2e, \quad \ldots \quad -1.065 \quad \ldots \quad (13)$$

$$2Cl^- \rightleftharpoons Cl_2\,(g) + 2e, \quad \ldots \quad -1.360 \quad \ldots \quad (14)$$

$$I^- + 3H_2O \rightleftharpoons IO_3^- + 6H^+ + 6e, \quad \ldots \quad -1.090 \quad \ldots \quad (15)$$

$$Br^- + 3H_2O \rightleftharpoons BrO_3^- + 6H^+ + 6e, \quad \ldots \quad -1.436 \quad \ldots \quad (16)$$

$$I_2 + 3H_2O \rightleftharpoons IO_3^- + 6H^+ + 5e, \quad \ldots \quad -1.200 \quad \ldots \quad (17)$$

$$Br_2 + 3H_2O \rightleftharpoons BrO_3^- + 6H^+ + 5e, \quad \ldots \quad -1.510 \quad \ldots \quad (18)$$

The E_o's for these oxidations are negative so that they are not spontaneous. By combining the E_o's suitably, one can get the following E.M.F's. for the complete cell reactions shown :

$$2MnO_4^- + I^- + 2H^+ \rightleftharpoons 2MnO_2 + H_2O + IO_3^-, \quad E_o = 0.500 \quad \ldots \quad (19)$$

$$2MnO_4^- + 6I^- + 8H^+ \rightleftharpoons 2MnO_2 + 4H_2O + 3I_2, \quad 1.253 \quad \ldots \quad (20)$$

$$2MnO_2 + 4I^- + 8H^+ \rightleftharpoons 2Mn^{2+} + 4H_2O + 2I_2, \quad 1.173 \quad \ldots \quad (21)$$

$$IO_3^- + 5I^- + 6H^+ \rightleftharpoons 3H_2O + 3I_2, \quad 0.753 \quad \ldots \quad (22)$$

$$2MnO_4^- + Br^- + 2H^+ \rightleftharpoons 2MnO_2 + H_2O + BrO_3^-, \quad 0.154 \quad \ldots \quad (23)$$

$$2MnO_4^- + 6Br^- + 8H^+ \rightleftharpoons 2MnO_2 + 4H_2O + 3Br_2, \quad 0.525 \quad \ldots \quad (24)$$

$$2MnO_4^- + 3HNO_2 \rightleftharpoons 2MnO_2 + H_2O + 3NO_3^- + H^+, \quad 0.650 \quad \ldots \quad (25)$$

$$MnO_2 + HNO_2 + H^+ \rightleftharpoons Mn^{2+} + NO_3^- + H_2O, \quad 0.570 \quad \ldots \quad (26)$$

By multiplying these E°'s by -23070 n one gets the corresponding decrease in free energy (cal. mole^{-1}). It is clear that there is no thermodynamic bar on the occurrence of reactions shown in (19) to (26). The equilibria in all cases are very favourable to completion of reduction. The poorest case appears in (23), but even here, $\log K = nE_o/0.059 = 6 \times 0.154/0.059$, whence $K = 4.58 \times 10^{15}$. In (20) similarly, $K = 2.63 \times 10^{27}$, a very complete reduction of permanganate indeed. In other cases the equilibrium constants have intermediate values.

In reductions by iodide, (20) shows the largest decrease in free energy, but is not observed to take place independently in any of the titrations so far. On the other hand, the corresponding reduction by bromide (24) is the only definite one in bromide titrations, 3 moles KBr per mole permanganate. Nitrite also produces this reduction, but only 1.5 moles of KNO_2 are consumed as is clear from the equation which has been set down above. It is clear that the reactions (19) to (26) are possible only in acid solutions, with the exception of (25).

In the reaction with KI, the decrease in free energy corresponding to (22) is quite distinct from that for (21). It should have been possible therefore to find

an inflection at 3.0 moles KI (0.5 for reaction 19 and 2.5 for reaction 22) and a final one at 5.0 moles. Only the latter of the two is observed in all titrations with KI. It appears therefore that the reduction after (19) may involve a mechanism by which one iodate and two MnO_2 molecules are simultaneously reduced by iodide. The inflection at 3.0 moles in the titration with bromide cannot be ascribed to the formation of bromate (reaction 23) followed by its reduction, since then, one would expect an initial inflection at 0.5 mole KBr.

Summarising, the reduction by KI in sulphuric acid solutions proceeds by the step (19), followed by (21) and (22) simultaneously. This is corroborated by the experimental observation that a dark brown precipitate (hydrated MnO_2) appears with the commencement of the titration and is followed by iodine only after 0.5 mole KI has been added. The filtrate at 0.5 mole KI on independent titration with KI requires 2.5 moles KI as expected, and the dark brown precipitate disappears at 5.0 moles KI, the mixture becoming practically colorless. These behaviours are unchanged in dilute hydrochloric acid solutions.

The first inflection in titrations with KI shifts to 0.66 mole in $N/2$ to $N/1$-H_2SO_4, and further to 0.84 mole in $5N$ to $6N$ acid. We were at first inclined to regard these shifts as an ill-defined approach to 1.0 mole KI. However, if the MnO_2 produced in (19) is at first reduced to Mn^{3+} and then to Mn^{2+}, and a corresponding quantity of iodide ions is oxidised to IO_3^-, it is easy to see that these shifts are quantitatively accounted for. This view is supported by the observation that the dark brown precipitate disappears before the final inflection (5 moles) in stronger sulphuric acid solutions.

When the titration is reversed and HCl is used in place of H_2SO_4, the first inflection is at 0.2 mole $KMnO_4$ per mole KI which, of course, corresponds to complete liberation of iodine and reduction of MnO_4^- to Mn^{2+}. As the titration is continued further, the iodine precipitated at first redissolves and another sharp inflection is observed at 0.4 mole $KMnO_4$. This corresponds to formation of ICl. In absence of excess $KMnO_4$, at any stage the iodide ion is unable to get oxidised to iodate as in the previous experiments. With KNO_2 the inflections are steady in dilute HCl solutions (1.5 moles, 2.5 moles KNO_2). The final inflection obviously corresponds to

$$2MnO_4^- + 5KNO_2 + 6H^+ \rightleftharpoons 2Mn^{2+} + 5KNO_3 + 3H_2O.$$

The shift observed in the first inflection (Fig. 5, H_2SO_4 mixtures) may again be ascribed to reduction of MnO_2 to Mn^{3+}, requiring half mole more of KNO_2. However, the shift is always less than this.

The behaviour of KBr, when the permanganate contains dilute HCl, is again simple, the only inflection being at 3.0 moles KBr; the reduction obviously follows reaction (24) since hydrated MnO_2 is formed and remains undissolved so that the final inflection corresponding to reduction to Mn^{3+} fails to appear. The behaviour in H_2SO_4 solutions is curious. Up to $2N$-H_2SO_4 the reaction fulfills all the requirements of (24). At about $4N$-H_2SO_4, there must be an approach to full reduction

of the MnO_2 to Mn^{2+}, but the reaction is complicated by evolution of oxygen. It seems that the MnO_2 is first reduced to Mn^{3+}, a part of which produces oxygen,

$$2Mn^{3+} + H_2O \rightleftharpoons 2Mn^{2+} + 2H^+ + O_2,$$

(no consumption of bromide) and the rest is reduced to Mn^{2+}, consuming KBr

$$Mn^{3+} + 2KBr \rightleftharpoons Mn^{2+} + 2K^+ + Br_2 \text{ (liq.)}.$$

Since the iodide ion is far easier to oxidise to iodine than water to H^+ and oxygen, the evolution of oxygen is not observed in the titrations with KI.

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SEARCH FOR NEW ANTISPASMODICS. PART IX

By T. N. Ghosh, Arun Bose and A. Raychaudhuri

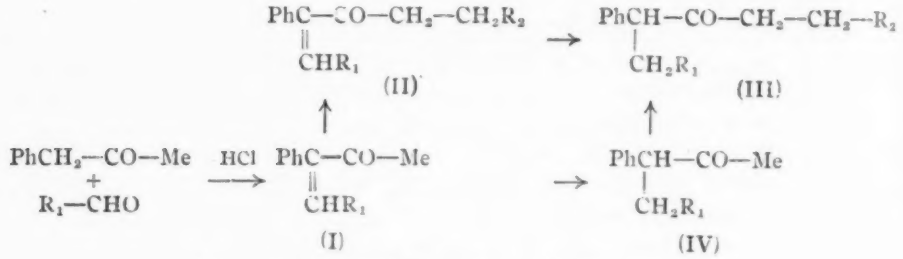
The Mannich bases (II and III) have been obtained. The site of the Mannich reaction with the ketone (IV) has been established.

In Part VIII (this *Journal*, 1959, **36**, 319 ; cf. *Proc. Indian Sci. Cong.*, 1959, Part III, p. 153) the synthesis of the Mannich base, 4-phenyl-4-benzyl-1 piperidino-butan-3-one, its derivatives and of the secondary alcohol therefrom has been recorded. It has also been reported that these compounds possess some antispasmodic activity, though rather toxic. In this connection reference is made to the observation of Marshall *et al.* (*Brit. J. Pharmacol. & Chemotherap.*, 1952, **7**, 85) that some β-dialkyl-aminoketones, chemically related to the above Mannich base, have been found to be spasmolytic, having non-specific direct action on plain muscle. In view of these observations, continued investigations dealing with the synthesis of such Mannich bases and their pharmacology appear to be warranted, and it has been felt desirable at this stage to have a methoxy substituent in the phenyl nucleus in such Mannich bases, since methoxy groups not only often confer enhanced biological activity but also greatly help in lowering the toxicity. Such a Mannich base, (III), has therefore been synthesised, following the same route as recorded previously (*loc. cit.*). Benzylmethyl ketone has been condensed with anisaldehyde in presence of hydrochloric acid (cf. Goldschmiedt and Krczmar, *Monatsh.*, 1897, **18**, 437 et seq) to furnish (I), which has been condensed with paraformaldehyde and piperidine to afford the Mannich base (II). On catalytic hydrogenation (II) has readily furnished the base (III).

A survey on the Mannich reaction indicates that compounds containing an active methyl or methylene or methynyl group undergo this reaction (Blicke, "Org. Reactions", 1947, Vol. 1, p. 308 et seq ; Alexander and Underhill, *J. Amer. Chem. Soc.*, 1949, **71**, 4014). So far as the relative activities of these are concerned, it is found as a general rule that the methylene group is more reactive than the methyl group in a Mannich reaction (Blicke, *loc. cit.*), and this probably prompted the supposition that the methynyl group is similarly more reactive than the methyl. Based on the latter assumption, the Mannich reaction with 1 : 1-diphenylacetone was considered by Jilek and Protiva (*Chem. Listy*, 1950, **44**, 49 ; *Chem. Abst.*, 1951, **45**, 7987) to have probably taken place at position-1. However, through a series of reactions and also degradation studies it has been established from three laboratories (Protiva and Jilek, *Coll. Czech. Chem. Comm.*, 1951, **16**, 151 ; Wilson and Kyi, *J. Chem. Soc.*, 1952, 1321 ; Katz and Karger, *J. Amer. Chem. Soc.*, 1952, **74**, 4085) that the Mannich reaction with 1 : 1-diphenylacetone takes place at position-3. These observations have now stimulated an enquiry to ascertain the site of the Mannich reaction in the case of a ketone of the type (IV), in which phenyl and substituted benzyl groups are attached to position-1. This ketone, obtained from the benzylidene

compound (I) by catalytic hydrogenation, has undergone the Mannich reaction with piperidine and paraformaldehyde to furnish the same base (III), as obtained by the unequivocal route (I-II-III). This has also been now confirmed in the case of the ketone (IV: R_1 = Ph) showing that in the present cases also the methyl group is more reactive than the methynyl, for the Mannich reaction.

Attempts to prepare the secondary alcohol from the aminoketone (III) by the use of aluminium propoxide[4] have failed. Probably some steric influence is involved.



(R_1 = *p*-methoxyphenyl ; R_2 = piperidino)

EXPERIMENTAL

1-Phenyl-1-(p-methoxy)-benzylidene-propan-2-one (I).—Anisaldehyde (41 g.) was dropwise added to a stirred solution of benzylmethyl ketone (40 g.) in ethanol containing a few drops of HCl (conc.). After the addition was over the mixture was stirred for 5 hours and then refluxed for 6 hours. The reaction mixture was taken up in ether and washed free of acid. The solution was dried (sodium sulphate) and the ether removed. The residual liquid was distilled under reduced pressure. After a forerun of anisaldehyde and benzylmethyl ketone, a colorless viscous liquid (20 g., b.p. 218-20°/8-10 mm) was collected. On chilling it solidified and was crystallised from petroleum ether (b.p. 60-80°) in colorless needles, m.p. 63-64°. (Found : C, 80.67; H, 6.41. $C_{17}H_{16}O_2$ requires C, 80.95 ; H, 6.35%).

The *semicarbazone* was crystallised from ethanol in colorless needles, m.p. 204-205°. (Found : N, 13.61. $C_{18}H_{19}O_2N_3$ requires N, 13.59%).

The *2:4-dinitrophenylhydrazone* was crystallised from butanol[n] in brown needles, m.p. 219-20°. (Found : N, 13.28. $C_{23}H_{20}O_5N_4$ requires N, 12.96%).

1-Phenyl-1-(p-methoxy)-benzylidene 4-piperidino-butan-2-one (II).—A mixture of (I, 18.6 g.), piperidine hydrochloride (15 g.), paraformaldehyde (3.6 g.), HCl (conc., 0.45 c.c.) and anhydrous ethanol (45 c.c.) was heated under reflux on the steam-bath for 12 hours. The solid obtained was washed with ether and then treated with excess of ammonia. The mass was extracted with ether and the ether extract washed with water and dried. Removal of the ether left a thick liquid (15 g.), which solidified on cooling. It was crystallised from petroleum ether (b.p. 40-60°) in brownish stout needles, m.p. 86-87°. (Found : C, 79.41 ; H, 7.62. $C_{23}H_{27}O_2N$ requires C, 79.08 ; H, 7.74%).

The *hydrochloride* was crystallised from ethanol in colorless, microcrystalline powder, m.p. 197-98°.

The *picrate* was crystallised from ethanol in yellow rectangular plates, m.p. 161-62°. (Found : N, 9.92. $C_{23}H_{27}O_2N$. $C_6H_3O_7N_3$ requires N, 9.69%).

The *oxalate* was crystallised from ethanol in colorless, rectangular plates, m.p. 181-82° (decomp.). [Found : N, 3.42. $C_{23}H_{27}O_2N$. $(CO_2H)_2$ requires N, 3.19%].

The *semicarbazone* separated on long standing and was crystallised from methanol in colorless, microcrystalline powder, m.p. 219-20°. (Found : N, 14.13. $C_{24}H_{30}O_2N_4$ requires N, 13.79%).

1-*Phenyl*-1-(p-*methoxy*)-*benzyl*-4-*piperidino*-*butan*-2-*one* (III).—Palladium-charcoal (10%, 0.1 g.) was added to a solution of (II, 6.3. g.) in ethanol (50 c.c.) and the mixture was shaken at room temperature with hydrogen at atmospheric pressure, when one equivalent of hydrogen was gradually absorbed and further absorption of hydrogen practically stopped. The catalyst was removed by filtration and washed with ethanol. The filtrate and washings were combined and removal of ethanol left a liquid, which was treated with HCl (dil.). The acid mixture was shaken with ether and the acid solution, when basified with ammonia, furnished the base, which was extracted with ether. The ether solution was dried (potassium carbonate) and removal of the ether left a viscous liquid.

The *hydrochloride* was crystallised from ethanol-ether mixture in colorless plates, m.p. 186-87°. (Found : N, 3.95 ; Cl, 9.68. $C_{23}H_{29}O_2N.HCl$ requires N, 3.61 ; Cl, 9.16%).

The *oxalate* was crystallised from ethanol in colorless plates, m.p. 161-62°. [Found : C, 68.48 ; H, 7.24. $C_{23}H_{29}O_2N$. $(CO_2H)_2$ requires C, 68.03 ; H, 7.03%].

1-*Phenyl*-1-(p-*methoxy*)-*benzylpropan*-2-*one* (IV)was obtained by catalytic hydrogenation of (I) over Pd-C and the method of procedure was the same as described above. The ketone, obtained as a viscous liquid, was characterised as 2 : 4-*dinitrophenylhydrazone*, which crystallised from acetone in deep red-coloured needles, m.p. 255-56°. (Found : N, 12.98. $C_{23}H_{22}O_5N_4$ requires N, 12.90%).

When the ketone (IV) was allowed to react with piperidine hydrochloride and paraformaldehyde in presence of ethanol and a trace of HCl (conc.), according to the procedure followed previously, a base was isolated as a viscous liquid, the hydrochloride and the oxalate of which were found to be identical in all respects with those of (III).

1-*Phenyl*-1-*benzylpropan*-2-*one* (IV : R_1 = phenyl) had been prepared by Goldschmiedt and Krczmar (*loc. cit.*) by reduction of (I : R_1 = phenyl) with sodium amalgam and characterised as oxime. However, the following catalytic reduction is found to be advantageous : Palladium-charcoal (10%, 0.3 g.) was added to a solution of (I : R_1 = phenyl ; 10 g.) in ethanol (75 c.c.) and the mixture was shaken at room temperature (*ca.* 33.5°) with hydrogen at atmospheric pressure, when one equivalent of hydrogen was absorbed and further absorption practically stopped. The catalyst was removed by filtration and, on removing ethanol from the filtrate, a thick liquid (10 g.) was obtained. The *semicarbazone* was crystallised from ethanol in colorless needles, m.p.

170-71°. (Found: N, 14.84. $C_{17}H_{19}ON_3$ requires N, 14.95%). The *oxime* had the same m.p as recorded by Goldschmiedt and Krczmar (*loc. cit.*).

When the above ketone was allowed to react with piperidine hydrochloride and paraformaldehyde in the usual way, a base was isolated as a heavy liquid, the derivatives (oxalate, semicarbazone and hydrochloride) of which were found to be identical in all respects with those of (III: R_1=phenyl ; R_2=piperidino), as recorded in Part VIII (*loc. cit.*).

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SPECTROPHOTOMETRIC DETERMINATION OF IRON WITH 3-HYDROXY-1-*p*-SULPHONATOPHENYL-3-PHENYLTRIAZINE

By H. K. L. Gupta and N. C. Sogani

Fe^{III} forms a bluish black water-soluble complex with 3-hydroxy-1-*p*-sulphonatophenyl-3-phenyl triazine in the *p*H range of 2.0 to 4.3, with absorption peaks at 520 and 650 mμ. Full colour development is ensured at 1 : 15 ratio of iron to the reagent. The system obeys Beer's law in the concentration range of 1 to 20 p.p.m. of iron The molecular extinction coefficient of iron complex at 650 mμ has been determined to be 4.47×10^3. Nessler's cylinder sensitivity has been found to be 1 part of iron in 5,000,000 parts of solution and spot plate identification limit as 0.1 γ iron in 0.15 c c. of solution.

3-Hydroxy-1-*p*-sulphonatophenyl-3-phenyltriazine has been reported as a spectrophotometric reagent for palladium (Sogani and Bhattacharyya, *Anal. Chem.*, 1957, **29**, 397) and molybdenum (unpublished). It develops an intense bluish black water-soluble colour with Fe (III). This property has been made use of successfully in the spectrophotometric determination of iron in presence of almost all the commonly associated diverse ions. 3-Hydroxy-1-phenyl-3-methyltriazine, possessing identical chelating system, has been recently described for the same purpose (Gupta and Sogani, this *Journal*, 1959, **36**, 87).

Experimental

Standard Fe(III) solution was prepared by oxidising 3.920 g. of ferrous ammonium sulphate (A.R.) with hydrogen peroxide in ammoniacal medium and dissolving the precipitated ferric hydroxide in HCl (dil.) before making up the volume to 1 litre (Clowes and Coleman, "Quantitative Chemical Analysis", 1947, p. 187). It was diluted to make a solution containing 25 p.p.m. of iron.

10% HCl (v/v) and 10% sodium acetate (w/v) solutions were used for adjusting the *p*H. A 0.4% reagent (w / v) solution in distilled water was used.

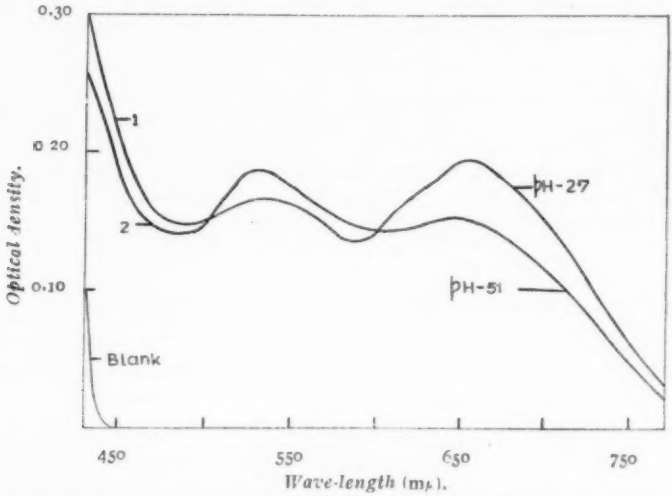
A Bausch and Lomb 'Spectronic-20' was used for measuring the absorption, using 1 cm cuvettes. *p*H measurements were made with a Beckman *p*H meter (model H-2). Visual colour comparisons were made with 50 c.c. Nessler's cylinders.

Absorption Spectra of Iron Complex and the Reagent.—Absorption spectra of 3-hydroxy-1-*p*-sulphonatophenyl-3-phenyltriazine and the chelates formed with Fe(III) at different *p*H values are shown in Fig. 1. Iron solutions (5 c.c. each containing 25 p.p.m.) were taken in two 50 c.c. flasks and varying amounts of HCl and sodium acetate solutions were added so that *p*H after dilution was 2.7 in one case and 5.1 in the other, followed by the reagent solution (10 c.c.), and the volume made up to the mark. Absorbance was measured with water as reference. A blank solution was prepared in a similar way and its absorbance was measured.

Inspection of the curves shows that at *p*H 2.7 (Fig. 1, curve 1), the absorbance is maximum at 650 mμ, and at *p*H 5.1 (curve 2), it is at 520 mμ. This variation in the nature of the curves is indicative of iron complexes of different compositions at different

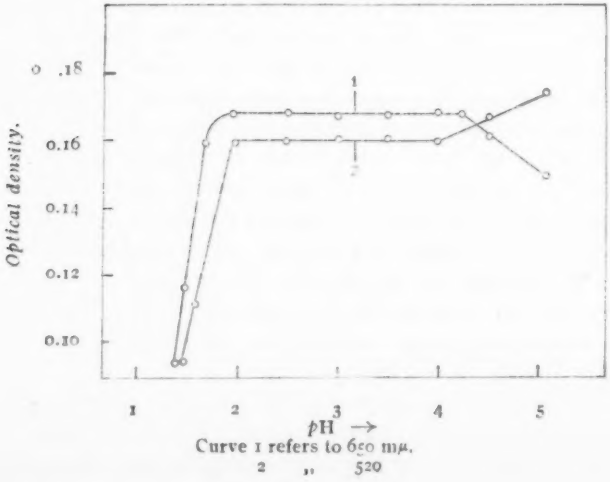
H^+-ion concentrations (Harvey and Manning, *J. Amer. Chem. Soc.*, 1950, **72**, 4488). 650 mμ was considered a suitable wave-length as there was no interference of the foreign ions in this region.

FIG. 1



Effect of pH on Degree of Complex Formation.—For studying the effect of *p*H on colour reaction, several solutions containing identical quantities of iron (4 c.c. of 25 p.p.m. iron) and the reagent were prepared, as given above, excepting that different amounts of HCl and sodium acetate solutions were added so that the final *p*H values ranged from 1.2 to 6.0. Absorbance was measured both at 650 and 520 mμ. Fig. 2 shows the effect of change of *p*H on complex formation. The range of constant maximum absorbance at 650 mμ is between *p*H 2.0 and 4.3. At 520 mμ,

FIG. 2



Curve 1 refers to 650 mμ.
2 ,, 520

the constant absorbance is between 2.0 and 4.0 and then it increases. It indicates the formation of an iron complex of different composition.

Effect of Reagent Concentration.—Varying amounts of $2 \times 10^{-3}M$ reagent solution were added to a series of solutions containing 5 c.c of $10^{-3}M$ iron. *p*H was kept at about 2.6. Absorbance was measured at 650 mμ, using water as blank. Full colour development was ensured at 1 : 15 ratio of iron to the reagent.

Development of Colour and Stability of the Complex.—The colour formation of the iron complex with the reagent was almost instantaneous and it retained stablity for 42 minutes at 22°. The blue colour of the complex changed to violet in about 4 hours. The fading of the colour is due to the reducing action of the reagent which converts ferric into ferrous and the change in colour is probably due to change in the composition of the complex.

Beer's Law.—Beer's law was obeyed in the concentration range of 1 to 20 p.p.m. of iron at 650 mμ. The molecular extinction coefficient of the iron complex has been calculated to be 4.47×10^3.

Effect of Temperature.—The colour intensity of the iron complex was slightly decreased with the increase in temperature. However, there was no appreciable difference within 10° of temperature.

Sensitivity of the Reaction.—Sensitivity of the reaction was determined in Nessler's cylinders in the usual way and was found to be 1 of iron in 5, 000, 000 parts of solution. Spot plate identification limit was found to be 0.1γ of iron.

Tolerance of Diverse Ions.—Qualitative testing has shown that As^{3+}, Sb^{3+}, Bi^{3+}, Al^{3+}, Cr^{3+}, Th^{4+}, Ce^{4+}, U^{4+}, UO_2^{2+}, Zr^{4+}, ZrO_2^{2+}, Pt^{4+}, Ru^{3+}, Rh^{4}, Ir^{3+}, alkali and alkaline earth metals and common anions do not show any colour reaction. There is no colour reaction with Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Pb^{2+}, Sn^{2+}, Sn^{4+} and Hg^{2+} at low *p*H, and these ions are not likely to interfere in the spectrophotometric determination of iron. Pd^{2+}, Cu^{2+}, Ti^{4+} and molybdate, which develop colour reactions with the reagent at low *p*H, show absorption only between 400 and 500 mμ and, hence, they do not interfere at 650 mμ in the determination of iron. Ag^{+} and Au^{3+} are slowly reduced by the reagent. Fluoride, phosphate, citrate, tartrate, oxalate and cyanide mask the colour reaction.

TABLE I

Tolerance of diverse ions.

Fe (III) = 4 p.p.m.

Ions.	Added as	Conc. of ion (p.p.m.)	Ions.	Added as	Conc. of ion.
Co^{2+}	Sulphate	100	Al^{3+}	Sulphate	100
Ni^{2+}	,,	100	Cr^{3+}	,,	20
Zn^{2+}	,,	100	Ca^{2+}	Chloride	100
Mn^{2+}	Chloride	100	MoO_4^{2-}	Sodium	50
Cu^{2+}	Sulphate	100	WO_4^{2-}	,,	100
Fe^{2+}	,,	100			

In examining the tolerance of various ions, only those elements, which normally occur with iron or are usually present in important alloys of iron, have been employed. Table I records the results obtained. Excepting for chromium and molybdate, where limiting concentrations have been found out, we have not tested the tolerance beyond the limit mentioned in the table.

Discussion

Fe(III) may be determined spectrophotometrically by various methods. Selection of the method of determination is not simple. The oldest and the best known is the one using thiocyanate (Ossian, *Pharm. Centr.*, 1837, **13**, 205). A more intense colour is obtained when the red colour is developed in 2-methoxyethanol (Winsor, *Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 453) or by adding 60% by volume of acetone (Woods and Mellon, *ibid.*, 1941, **13**, 551). Other reagents used are 7-iodo-8-hydroxyquinoline-5-sulphonic acid (Yoe and Hall, *J. Amer. Chem. Soc.*, 1937, **59**, 872), nitroso-dimethyldihydroresorcinol (Shome, *Anal. Chem.*, 1948, **20**, 1205), disodium 1:2-dihydroxybenzene-3:5-disulphonate (Yoe and Jones, *Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 111), salicylic acid, salicylaldoxime, etc.

Numerous new reagents continue to be proposed. The following have been selected as most worthy of mention, which are reported during the last 4 years. Fe (III) develops a red colour with 3-sulphoanthranilic acid (Zehner and Sweet, *Anal. Chem.*, 1956, **28**, 198), purple colour with 2-fluorobenzoic acid (Buchanan aud Wagner, *ibid.*, 1957, **29**, 754), red-violet colour with ethylenediamine-*bis* (sulphosalicylaldehyhe) (Mukherjee, *Anal. Chim. Acta*, 1955, **13**, 268), red colour with thenoyltrifluoroacetone (Kingdom and Mellon, *Anal. Chem.*, 1956, **28**, 860) and blue colour with 4-amino-4-methoxydiphenylamine (Erdey and Szabadvary, *Acta Chim. Acad. Sci. Hung.*, 1955, **6**, 131). 3-Hydroxy-1-*p*-sulphonatophenyl-3-phenyltriazine is one more addition to the list of good spectrophotometric reagents for iron. No claim for its superiority over other reagents is made.

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STUDIES ON THE PRECIPITATION OF INVERTASE BY ALCOHOL-WATER MIXTURES

By M. M. Biswas

Yeast invertase has been precipitated at different *p*H values by ethanol-water mixtures consisting of 10 to 60% alcohol in the cold (at 0°-5°). At *p*H 4.5, the optimum *p*H for enzyme reaction of invertase, the influence of dissolved ions in the precipitation of the enzyme protein is also recognised. Although higher percentage of ethanol, viz., 60%, affords better yield of the precipitate, there is an optimum percentage of alcohol. viz , 50%, for precipitation of invertase of ideal activity at the optimum *p*H 4.5.

Influence of different salts on the invertase activity of yeast has been recorded in a previous paper (this *Journal*, 1956, **33**, 815). The invertase preparations used for the experiments were made from samples of autolysed Brewer's yeast mixture after filtration with kieselguhr and subsequent dialysis. In this process the enzyme protein was not subjected to any further treatment for purification or crystallisation. The work of Cohn *et al.* (*J. Amer. Chem. Soc.*, 1946, **68**, 459) regarding the fractionation of normal human plasma by precipitation with ethanol-water mixture in the cold suggested another practical method for purifying biologically active proteins. Their method eliminated the process of dialysis, necessary for the removal of ammonium sulphate, generally used for fractionation of the plasma. They removed the alcohol by evaporation under reduced pressure in the cold. The dangers of bacterial growth, which beset dialysis, are completely avoided in this method. An attempt has been made in the present investigation to crystallise the invertase protein from yeast extract according to this method, and some studies have been made on the protein-electrolyte interactions in presence of alcohol in the cold. The influence of *p*H on the optimum precipitation of the enzyme protein according to this new method has been studied.

An attempt has been made to correlate this optimum precipitation of the enzyme protein with the total invertase activity of the precipitate. The aim of the present series is to ascertain an optimum *p*H and percentage of alcohol for the crystallisation of invertase in the pure state with the maximum output of enzyme activity.

Experimental

The invertase extract was first prepared according to the method of Adams and Hudson (*J. Amer. Chem. Soc.*, 1943, **65**, 1959) by prolonging the period of autolysis to 4 days. Dried Brewer's yeast powder (220 g.) was treated with toluol (22 c.c.) and distilled water (330 c.c.), and the mixture was kept at 35° for 4 days. After this period of autolysis, the mixture was diluted with water (300 c.c.) and filtered with kieselguhr under suction. The clear filtrate was put to a dialyser at 35°, fed with running tap water and dialysis carried on for 48 hours, using toluol in the bags to prevent putrefaction. Percentage of protein in the invertase filtrate was found to

be 1.39. The enzyme extract (10 c.c.) was mixed with 40 c.c. mixtures of ethanol and water. Percentage of ethanol varied from 10.0 to 60.0. Precipitation was made in the cold in the frigidaire, the temperature of which varied between 0° and 5°. Precipitate, after filtration under suction in the cold, was dried in vacuum and weighed as such. The specimen, so obtained, is likely to contain different types of proteins, both active and inactive, but otherwise the material is of sufficient purity and the observed behaviour relates to this purified specimen as a whole. Experiments were performed in a range of *p*H varying between 3.5 and 7.0. The results have been recorded in Table I (A F). Precipitates of the various protein-alcohol mixtures were centrifuged and after decantation of the supernatant liquid tested for their enzyme activity in the usual manner. The *p*H values between 3.5 and 7.0 and the percentages of alcohol between 10.0 and 60.0 were correlated with the invertase activity of 10 g. invertase extract in each case. The results are recorded in Table II and in Fig. 1.

TABLE I

Invertase extract: 10 c.c. Alcohol-water mixture: 40 c.c.

Protein precipitated at different *p*H.

% EtOH.	A. *p*H 3.5.	B. *p*H 4.0.	C. *p*H 4.5.	D. *p*H 5.0.	E. *p*H 6.0.	F *p*H 7.0.
10.0	0.0041 g.	0.0117 g.	0.0031 g.	0.0030 g.	0.0030 g.	0.0158 g.
15.0	0.0092	0.0294	0.0080	0.0100	0.0140	0.0154
20.0	0.0096	0.0302	0.0080	0.0132	0.0138	0.0174
25.0	0.0064	0.0310	0.0144	0.0210	0.0132	0.0165
30.0	0.0130	0.0340	0.0162	0.0244	0.0148	0.0132
35.0	0.0122	0.0340	0.0122	0.0246	0.0190	0.0160
40.0	0.0168	0.0280	0.0166	0.0270	0.0128	0.0160
50.0	0.0342	0.0446	0.0380	0.0652	0.0594	0.0728
60.0	0.0420	0.0514	0.0550	0.0706	0.0744	0.0904

TABLE II

Invertase activity at different percentages of alcohol and pH values.

Invertase extract used: 10 c.c. (% protein = 1.39).

Substrate: 80 g. sucrose in 200 c.c. water.

Invertase activity in g. glucose by 10 g. yeast extract at diff. *p*H values.

% EtOH.	*p*H 3.5.	*p*H 4.0.	*p*H 4.5.	*p*H 5.0.	*p*H 6.0.	*p*H 7.0.
10.0	27.7	89.9	109.4	98.7	89.9	85.2
15.0	29.7	86.1	112.3	107.9	95.2	87.07
20.0	29.9	98.7	147.2	119.04	107.9	89.9
25.0	29.7	103.7	161.8	126.5	109.4	91.9
30.0	31.1	107.9	161.8	139.5	115.6	98.7
35.0	33.7	112.3	168.6	144.6	119.04	101.1
40.0	35.1	119.04	176.05	150.0	122.6	103.7
50.0	36.7	122.6	231.4	155.8	126.5	109.4
60.0	36.7	124.5	231.4	161.8	130.6	112.5

Discussion

Influence of H^+-ion concentration on the precipitation of enzyme protein from a solution of invertase from Brewer's yeast by alcohol has been recorded in Table I. To avoid denaturation of the precipitated protein, cold conditions have been maintained (0°-5°). Cohn *et al.* (*loc. cit.*) carried out their experiments on fractionation of human plasma in a comparatively cold zone (0°-10°). The condition of precipitation is, however, quite satisfactory in the present instance. The range of H^+-ion concentration varies between *p*H 3.5 and 7.5 and that of ethanol concentration, between 10.0% and 60.0%. Evidently the optimum precipitation of enzyme protein has been observed in the protein-alcohol mixture at *p*H 4.5. It may be noted that only two variables have been studied in the protein precipitation reactions. These are the ethanol concentration and the H^+-ion concentration. It is evident from Table I that in the range of ethanol concentrations between 10% and 40%, the amount of protein precipitation is rather low, whereas at 50% and 60% concentrations of alcohol, the amounts of the precipitate are appreciably high.

Fig. 1

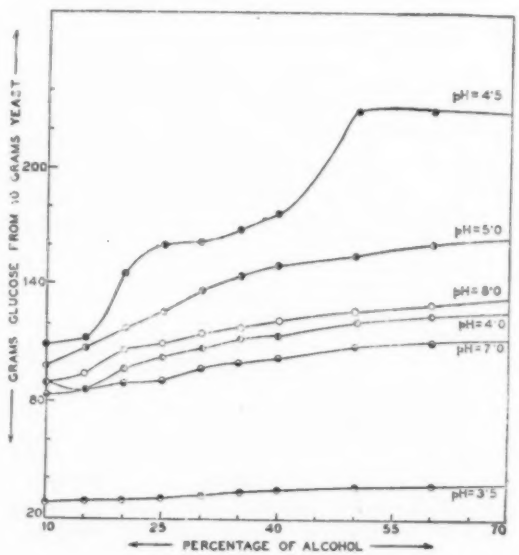

Fig. 1 (vide Table II) illustrates the variation of invertase activity of enzyme extracts with the percentage of alcohol used for precipitation of the enzyme at *p*H values ranging between 3.5 and 7.0. It is evident from the steepness of the curve at *p*H 4.5 that for the same percentage of alcohol used, precipitates at this *p*H possess superior invertase activity. Enzyme activity, as measured in terms of g. glucose formed by 10 g. of invertase extract, attains almost a maximum at this *p*H (4.5) and at 50% alcohol strength. It is significant that at *p*H 4.5, the influence of dissolved ions in the precipitation of the enzyme protein has already been recognised. The

present experiments establish beyond doubt that mere precipitation is not the criterion of activity, and the activity of the precipitate is not proportional to the mass. Thus, it is apparent from Table II that activity increases by about one-third its value with increase of percentage of alcohol from 10.0 to 60.0. Alcohol precipitation figures (vide Table I) indicate that amount of protein precipitate increases in some cases about twenty times for the above range (10.0% to 60.0% alcohol). It is therefore possible from the present series of investigations to contemplate an optimum *p*H (4.5) as also an optimum percentage of alcohol (50.0) for precipitation of invertase of ideal activity.

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STUDIES ON THIOPHOSPHORYL CHLORIDE AS A SOLVENT. PART I

By Ram Chand Paul, Kailash Chander Malhotra and Gurdev Singh

An attempt has been made to exploit the potentialities of thiophosphoryl chloride as a solvent for chemical reactions. The results show that the Lewis acids are fairly soluble in this solvent. Neutralisation reactions between the solvo-acids and solvo-bases have been studied and complexes formed have been isolated and analysed

In view of phosphoryl chloride being quite extensively studied as a non-aqueous solvent, an endeavour has been made to explore the potentialities of thiophosphoryl chloride as a solvent for chemical reactions. Thiophosphoryl chloride hydrolyses more slowly than phosphoryl chloride and yields phosphoric acid, hydrochloric acid, hydrogen sulphide and, perhaps, a little sulphur, which makes the solution slightly turbid.

$$PSCl_3 + 4H_2O \longrightarrow H_3PO_4 + H_2S + 3HCl.$$

Its dielectric constant (5.8 at 21.5° ; cf. acetic acid, 6 at 25° and carbonyl chloride, 4.34 ± 0.02° at 22°) and easy working range (m. p. −35° to b.p. 125°) make its study as a solvent quite convenient. The electron diffraction data for thiophosphoryl chloride (Beach and Stevenson, *J. Chem. Phys.*, 1938, **6**, 75) show that its structure is the same as that of its oxygen analogue. Radio-chlorine exchange reactions (Masters, Potters, Asher and Norris, *J. Amer. Chem. Soc.*, 1956, **78**, 4252 ; Lewis and Sowerby, *J. Chem. Soc.*, 1957, 336) have confirmed the ionisation of phosphoryl chloride as :

$$POCl_3 \rightleftharpoons POCl_2^+ + Cl^-$$
$$POCl_3 + Cl^- \rightleftharpoons POCl_4^-.$$

By analogy, it can be safely assumed that thiophosphoryl chloride ionises as

$$PSCl_3 \rightleftharpoons PSCl^+_2 + Cl^-.$$

As a first step towards the study of this solvent, the solubilities of a number of substances have been determined quantitatively at 35° ± 0.1°. The results recorded in Table I show that the Lewis acids are fairly soluble in thiophosphoryl chloride. The production of coloured solutions in some of these cases is indicative of the formation of complexes in solution. Strongly electrovalent chlorides are insoluble, and this fits in well with the common observation that in solvents with low dielectric constants, the covalent compounds are more soluble than the electrovalent ones. Qualitative tests have shown that the solubilities of the trichlorides of antimony, iron, bismuth and aluminium in thiophosphoryl chloride increase with rise in temperature. A qualitative study of the solubilities also reveals that dimethylaniline and γ-picoline are very soluble ; quinoline, pyridine, α-picoline, β-picoline and antimony pentachloride are moderately soluble ; while zirconium and tellurium tetrachlorides are only slightly soluble in this solvent.

TABLE I

Solubilities of chlorides in thiophosphoryl chloride at 35° ± 0.1°.

Chlorides.	Solubility (g./100 g. of solvent).	Colour of soln.	Chlorides.	Solubility (g./100 g. of solvent)	Colour of soln.
$AlCl_3$	30.65	Light yellow	$FeCl_3$	7.26	Greenish red
$SnCl_4$	Miscible	Colorless	$AsCl_3$	Miscible	Colorless
NaCl	Insoluble	,,	NH_4Cl	Insoluble	,,
$SbCl_3$	125.30	,,	$BaCl_2$	Insoluble	,,
$TiCl_4$	Miscible	Yellow	$BiCl_3$	0.52	,,
KCl	Insoluble	Colorless	BCl_3	Miscible	,,
LiCl	Insoluble	,,			

N B. Insoluble refers to a solubility of less than 0.1%

Formation of Solvates.—A number of compounds were studied for the purpose of solvate formation in thiophosphoryl chloride, but only aluminium chloride and antimony pentachloride have been found to furnish monosolvates. Aluminium chloride dissolves in thiophosphoryl chloride on heating. On cooling the saturated solution, a yellowish white crystalline monosolvate, $AlCl_3.PSCl_3$, separates out (m.p. 115°, decomp.). Antimony pentachloride forms a reddish brown crystalline monosolvate, $SbCl_5.PSCl_3$, when the two liquids are mixed (m.p. 101°, decomp.).

Stannic chloride, titanium tetrachloride, arsenic trichloride and boron trichloride are miscible with thiophosphoryl chloride in all proportions. All efforts to separate any solid solvates were unsuccessful. Antimony trichloride, although highly soluble in thiophosphoryl chloride, does not yield any solvate. Pure crystals of antimony trichloride separate out when its saturated solution in the solvent is cooled. Zirconium tetrachloride, tellurium tetrachloride, bismuth trichloride and ferric chloride, which are slightly soluble, also do not furnish any solvates with this solvent. Sulphur trioxide reacts chemically with the solvent, resulting in the separation of sulphur. It was also not possible to isolate the solid solvates of quinoline, pyridine, α-, β- and γ-picolines and dimethylaniline, although some of them developed a slight turbidity in solution with thiophosphoryl chloride.

Acid-base Neutralisation Reactions.—On the basis of the assumption that thiophosphoryl chloride ionises, as indicated above, all substances, which on dissolution in this solvent increase the concentration of $PSCl_2^+$, will act as acids and those which increase the concentration of Cl^- will act as bases. Lewis acids, e.g., antimony pentachloride, antimony trichloride, aluminium chloride, stannic chloride and titanium tetrachloride, which have a tendency to increase their co-ordination number, can combine with the chloride ions so as to release the $PSCl_2^+$, and thus act as solvo-acids, whereas the organic tertiary bases, quinoline, pyridine, α-, β- and γ-picolines, which contain electron-donor nitrogen atoms, can combine with $PSCl_2^+$ and thus increase the concentration of chloride ions and act as solvo-bases in thiophosphoryl chloride.

TABLE II

Acid-base neutralisation complexes isolated in thiophosphoryl chloride.

Acid.	Base.	Complex isolated.	Colour.	M.P.*	%Metal. Found.	%Metal. Calc.	%Chlorine. Found	%Chlorine. Calc.	%Sulphur. Found	%Sulphur. Calc.	%Base. Found.	%Base. Calc.
$SbCl_5$	Quinoline	$(C_9H_7N.PSCl_2)SbCl_6$	Brown	150-53°	20.36	20.37	47.68	47.50	5.50	5.35	20.37	21.57
,,	Pyridine	$(C_5H_5N.PSCl_2)SbCl_6$	,,	120-22°(d)	22.47	22.23	51.68	51.84	5.83	5.84	13.60	14.40
,,	β-Picoline	$(C_6H_7N.PSCl_2)SbCl_6$	Reddish brown	142-43°(d)	21.32	21.68	50.67	50.57	5.54	5.69	15.85	16.55
$AlCl_3$	Quinoline	$(C_9H_7N.PSCl_2)AlCl_4$	White	100-102°	6.25	6.24	49.10	49.05	7.53	7.63	30.25	29.81
,,	Pyridine	$(C_5H_5N.PSCl_2)AlCl_4$	,,	133-35°	7.36	7.07	55.80	55.75	7.98	8.37	22.12	20.65
$SbCl_3$	Pyridine	$(C_5H_5N)SbCl_3$	,,	160-62°	39.46	39.67	34.92	34.65	...	...	25.52	25.48
$SnCl_4$	Quinoline	$(C_9H_7N.PSCl_2)_2SnCl_6$	,,	200°(d)	13.88	13.83	41.87	41.39	8.02	7.46	27.65	30.08
,,	Pyridine	$(C_5H_5N)_2SnCl_4.PSCl_3$	,,	...	19.85	20.18	42.30	42.24	5.23	5.44	23.02	26.86
,,	α-Picoline	$(C_6H_7N)_2SnCl_4.PSCl_3$	Pale yellow	160-62°	19.05	19.26	40.33	40.32	5.20	5.19	32.95	30.18
,,	γ-Picoline	$(C_6H_7N)_2SnCl_4.PSCl_3$	White	180°	19.21	19.26	40.57	40.32	5.26	5.19	26.73	30.18
$TiCl_4$	Quinoline	$(C_9H_7N.PSCl_2)TiCl_5$	Orange-red	210-15°	9.93	9.80	51.13	50.88	5.86	6.55	20.16	26.42
,,	Pyridine	$(C_5H_5N)_2TiCl_4.PSCl_3$	Yellow	175-79°(d)	9.15	9.25	48.12	48.02	6.01	6.16	30.01	30.57

*Melting points are uncorrected (d- denotes decomposition).

The structure of the solvo-acids and bases in thiophosphoryl chloride, just as it has been represented in acetyl chloride (Paul, Singh and Sandhu, *J. Chem. Soc.*, 1959, 315) and benzoyl chloride (Paul, Chander and Singh, this *Journal*, 1958, **35**, 869), can be represented as:

$$PSCl_3 + AlCl_3 \rightarrow PSCl_3.AlCl_3 \rightleftharpoons (PSCl_2)^+(AlCl_4)^- \rightleftharpoons PSCl_2^+ + AlCl_4^-$$

or $$B + PSCl_3 \longrightarrow B.PSCl_3 \rightleftharpoons (B.PSCl_2)^+ (Cl)^- \rightleftharpoons (B.PSCl_2)^+ + Cl^-,$$

where B represents all the tertiary organic bases. $AlCl_3$ is a typical Lewis acid and $SbCl_5$ and other Lewis acids also will behave similarly.

Neutralisation reactions between these solvo-acids and bases have been studied and the complexes, recorded in Table II, have been isolated and analysed. It has been found that antimony pentachloride, antimony trichloride and aluminium chloride act as monobasic acids while the tetrachlorides of tin and titanium act as dibasic acids. Some of theses complexes, however, lose solvent molecules to yield desolvated products.

Antimony pentachloride forms a monosolvate, $SbCl_5.POCl_3$, with phosphoryl chloride (Gutmann, *Z. anorg. allgem. Chem.*, 1952, **270**, 179). The Raman spectrum of this compound (Gutmann, *Monatsh.*, 1958, **86**, 52) shows the presence of $SbCl_6^-$ and indicates the structure of the compound to be $(POCl_2)^+(SbCl_6)^-$. By analogy, the ionisation of $SbCl_5.PSCl_3$ in thiophosphoryl chloride may be assumed to take place as:

$$SbCl_5.PSCl_3 \rightleftharpoons PSCl_2^+ + SbCl_6^-.$$

Brown crystalline complexes: $(C_9H_7N.PSCl_2)SbCl_6$, $(C_5H_5N.PSCl_2)SbCl_6$ and $(C_6H_7N.PSCl_2)SbCl_6$ are isolated when a solution of antimony pentachloride in thiophosphoryl chloride is allowed to react with the solutions of quinoline, pyridine, and β-picoline respectively in thiophosphoryl chloride. The reactions may be represented as:

$SbCl_5 + PSCl_3 \longrightarrow SbCl_5.PSCl_3 \rightleftharpoons PSCl_2^+ + SbCl_6^-$ (Formation and ionisation of the solvo-acids).

$B + PSCl_3 \longrightarrow B.PSCl_3 \rightleftharpoons (B.PSCl_2)^+ + Cl^-$ (Formation and ionisation of solvo-base).

$PSCl_2^+ + SbCl_6^- + (B.PSCl_2)^+ + Cl^- \longrightarrow (B.PSCl_2)SbCl_6 + PSCl_3$ (Neutralisation, B stands for base).

Aluminium chloride, which forms a monosolvate, reacts with quinoline and pyridine in thiophosphoryl chloride solutions to yield white crystalline complexes, $(C_9H_7N.PSCl_2)AlCl_4$ and $(C_5H_5N.PSCl_2)AlCl_4$ respectively. Their formation may be explained as:

$$AlCl_3 + PSCl_3 \longrightarrow AlCl_3.PSCl_3 \rightleftharpoons PSCl_2^+ + AlCl_4^-$$

$$PSCl_2^+ + AlCl_4^- + (B.PSCl_2)^+ + Cl^- \longrightarrow (B.PSCl_2)AlCl_4 + PSCl_3.$$

A white crystalline complex is isolated when a solution of antimony trichloride in thiophosphoryl chloride is neutralised with a solution of pyridine in the same solvent. This complex after drying in vacuum was analysed. The results agreed with the formula, $C_5H_5N.SbCl_3$. Its formation may be represented as:

$$SbCl_3 + PSCl_3 \rightleftharpoons PSCl_2^+ + SbCl_4^-$$

$$PSCl_2^+ + SbCl_4^- + (B.PSCl_2)^+ + Cl^- \longrightarrow (B.PSCl_2)\,SbCl_4 + PSCl_3.$$

On drying under vacuum, the complex loses a molecule of the solvent to afford the desolvated product,

$$(B.PSCl_2)SbCl_4 \longrightarrow B.SbCl_3 + PSCl_3.$$

Stannic chloride and titanium tetrachloride have been used as solvo-acids in a number of non-aqueous solvents. In most of these cases they form complexes with organic tertiary bases or quaternary ammonium halides, which contain hexachlorostannate and hexachlorotitanate ions. Stannic chloride forms complexes of the formulae: $(C_9H_7N.PSCl_2)_2SnCl_6$, $(C_5H_5N)_2SnCl_4.PSCl_3$, $(\alpha\text{-}C_6H_7N)_2SnCl_4.PSCl_3$ and $(\gamma\text{-}C_6H_7N)_2SnCl_4.PSCl_3$ with quinoline, pyridine, α-picoline and γ-picoline respectively in thiophosphoryl chloride solutions. The reactions can be represented as:

$$SnCl_4 + 2PSCl_3 \rightleftharpoons 2(PSCl_2)^+ + (SnCl_6)^{2-}$$

$$2(PSCl_2)^+ + (SnCl_6)^{2-} + 2(B.PSCl_2)^+ + 2Cl^- \longrightarrow (B.PSCl_2)_2SnCl_6 + 2PSCl_3.$$

The complexes formed by the last three bases lose a molecule of the solvent to yield the partially desolvated products.

$$(B.PSCl_2)_2SnCl_6 \longrightarrow B_2.SnCl_4.PSCl_3 + PSCl_3.$$

Titanium tetrachloride on reaction with quinoline in thiophosphoryl chloride solution yields an orange-red acid salt, which has been analysed in partially desolvated form, $(C_9H_7N.PSCl_2)TiCl_5$. Its formation can be explained on the basis of the formation and subsequent desolvation of the acid salt, $(C_9H_7N.PSCl_2)(PSCl_2)TiCl_6$ under vacuum as:

$$TiCl_4 + 2PSCl_3 \rightleftharpoons 2(PSCl_2)^+ + (TiCl_6)^{2-}$$

$$(B.PSCl_2)^+ + Cl^- + 2(PSCl_2)^+ + (TiCl_6)^{2-} \longrightarrow (B.PSCl_2)(PSCl_2)TiCl_6 + PSCl_3$$

$$(B.PSCl_2)(PSCl_2)TiCl_6 \longrightarrow (B.PSCl_2)TiCl_5 + PSCl_3.$$

With pyridine, titanium tetrachloride furnished a normal salt, which was analysed in a partially desolvated state, $(C_5H_5N)_2TiCl_4.PSCl_3$.

$$2(B.PSCl_2)^+ + 2Cl^- + 2PSCl_2^+ + TiCl_6^{2-} \longrightarrow (B.PSCl_2)_2TiCl_6 + 2PSCl_3$$

$$(B.PSCl_2)_2TiCl_6 \longrightarrow B_2.TiCl_4.PSCl_3 + PSCl_3.$$

The conductometric studies in this solvent are in progress.

EXPERIMENTAL

Thiophosphoryl chloride was prepared by the aluminium chloride-catalysed reaction of phosphorus trichloride with sulphur (Knotz, *Oesterr. Chem.-Ztg.*, 1949, **50**, 128) and purified by repeated fractional distillation in a special fractionating column, the distillate being collected at a take off ratio of 1:5. Aluminium chloride was purified by subliming in a current of dry chlorine, while anhydrous antimony trichloride was purified by distillation. All other materials were purified by the methods described previously (Paul *et al.*, *loc. cit.*).

The procedure adopted for the determination of the solubilities at 35° ± 0.1° was the same as described for benzoyl chloride (Paul, Bains and Singh, this *Journal*, 1958, **35**, 489).

Preparation of Solvates.—Antimony pentachloride (5 g.) was added dropwise to 20 c.c. of thiophosphoryl chloride, placed in a conical flask, fitted with a dropping funnel and a calcium chloride guard tube. The reaction mixture was stirred with the help of a magnetic stirrer. A reddish brown solid separated out with the evolution of heat. This was filtered in a dry atmosphere, washed with dry petroleum ether (40-60°) and dried under vacuum. The analysis conformed to the formula, $SbCl_5.PSCl_3$; yield 5.5 g. (Found: Sb, 25.64; Cl, 59.75; S, 6.24. $SbCl_5.PSCl_3$ requires Sb, 25.91; Cl, 60.55; S, 6.83%).

Anhydrous aluminium chloride (5 g.) was dissolved in hot thiophosphoryl chloride (20 c.c.). The solution was filtered hot in a dry atmosphere and allowed to cool, when a yellowish white crystalline solid separated out. This was filtered, washed with dry petroleum ether (40-60°) and dried under vacuum, yield 2 8 g. (Found: Al, 9.04; Cl, 70.19; S, 10.10. $AlCl_3.PSCl_3$ requires Al, 8.91; Cl, 70.30; S, 10.55%).

Preparation of Neutralisation Complexes.—Equivalent amounts of the respective acid and base were dissolved in thiophosphoryl chloride separately. In general, the acid solution was added dropwise to the base solution in an apparatus, already mentioned under preparation of solvates. In the case of complex formation with antimony pentachloride, however, a reverse procedure was followed. The solid, thus separated, was filtered in a dry atmosphere, washed successively with thiophosphoryl chloride and dry petroleum ether (40-60°), and dried under vacuum. For determination of the percentage of the base in the complex, a known weight of the complex was dissolved in 15 c.c. of anhydrous acetic acid, prepared for non-aqueous titrations. About 0.5 g. of mercuric acetate and a drop of crystal violet indicator in anhydrous acetic acid were added and the solution titrated against $N/10$ perchloric acid in anhydrous acetic acid. A greenish blue colour indicated the end-point.

The acid-base complexes, thus prepared, are recorded in Table II along with their analytical data, colour and melting points, etc.

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*iso*QUINOLINE DERIVATIVES. PART VI

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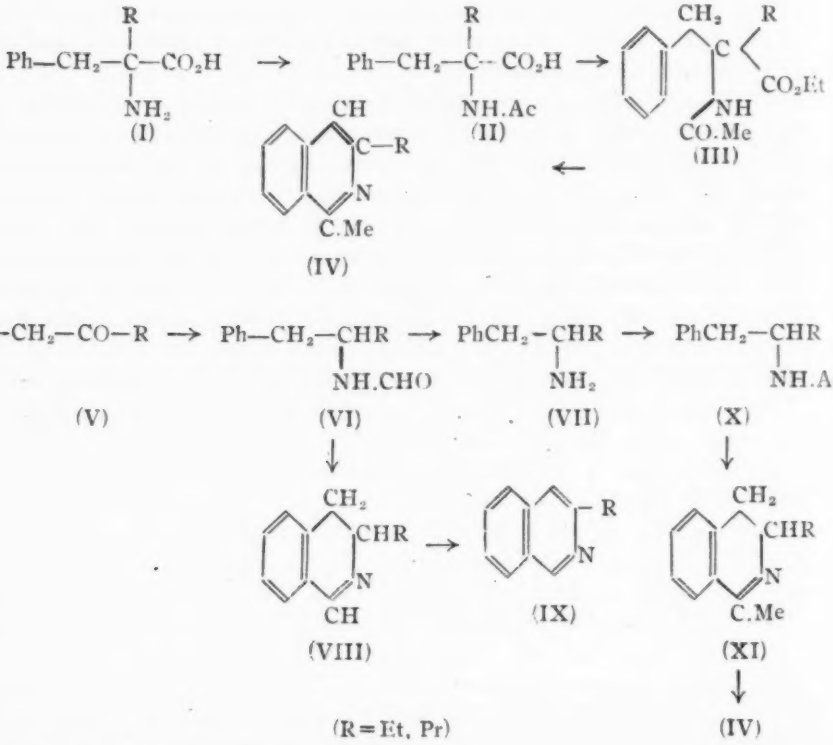
As in the case of ethyl α-methyl-α-acetamido-β-phenylpropionate (Part V, this *Journal*, 1959, **36**, 425), the corresponding α-ethyl or α-propyl analogue has furnished, when treated with P_2O_5 in an inert solvent, 1-methyl-3-ethyl (or propyl)-*iso*quinoline, the structure of which has been confirmed by an independent synthesis.

In Part V (this *Journal*, 1959, **36**, 425) it has been recorded that ethyl α-methyl-α-acylamido-β-phenylpropionate, when subjected to the Bischler-Napieralski cyclisation with phosphorus pentoxide in an inert solvent, yields 1-alkyl-3-methyl*iso*quinoline. This reaction is of interest in that it apparently involves, in one operation, cyclodehydration, decarbonylation and dehydrogenation, and has been found to be realised when the nature of the acylamido group is varied. However, it has been indicated that the presence of a quaternary carbon atom in the above ester might promote this facile reaction, and consequently it has now been considered desirable to ascertain, in this respect, the influence of substituents attached to this quaternary carbon atom. Extension of work along this line might render possible an assessment regarding the general applicability of the reaction.

α-Amino-α-ethyl (or propyl)-β-phenylpropionic acid (I), obtained by alkaline hydrolysis of 5-benzyl-5-ethyl (or propyl)-hydantoin, has been acetylated to furnish (II). The ester (III), obtained from (II), has been subjected to the Bischler-Napieralski cyclisation with phosphorus pentoxide in presence of an inert solvent, when a base, agreeing on analysis with (IV), has been obtained. The structure (IV) has been established by an independent synthesis: Benzylethyl (or propyl) ketone (V) has been converted into the amine (VII) by the Leuckart procedure (cf. Ingersoll *et al.*, *J. Amer. Chem. Soc.*, 1936, **58**, 1808). The intermediate *N*-formyl derivative (VI) has been isolated and hydrolysed to the free base (VII). Although the amine (VII) may be accessible through other routes, previously recorded (Rosenmund *et al.*, *Ber.*, 1942, **75B**, 1850; Kornblum and Iffland, *J. Amer. Chem. Soc.*, 1949, **71**, 2137; Pohland and Sullivan, *ibid.*, 1953, **75**, 5893; Ishiwata and Suzuki, *J. Pharm. Soc. Japan*, 1951, **71**, 1263), it has been found to be of advantage to apply the Leuckart procedure to obtain the same. The possibility of utilising (VII) for the synthesis of (IV) with such a substitution as ethyl or propyl in 3-position has been tested by subjecting (VI) to the action of a mixture of phosphorus oxychloride and polyphosphoric acid to furnish 3-ethyl (or propyl)-3:4-dihydro*iso*quinoline (VIII). (VIII) has been dehydrogenated over Pd—C to furnish 3-ethyl (or propyl)-*iso*quinoline (IX), previously prepared through different routes (Damerow, *Ber.*, 1894, **27**, 2237; Albahary, *Ber.*, 1896, **29**, 2397). Accordingly, (VII) has been acetylated and the acetyl derivative (X), when treated with phosphorus oxychloride in an inert solvent, has furnished 1-methyl-3-ethyl (or propyl)-3:4-dihydro*iso*quinoline (XI). On dehydrogenation over Pd—C, (XI) has readily furnished (IV).

It is, thus, evident that with such a substitution as methyl, ethyl or propyl in the quaternary carbon atom in (III), the fully aromatised *iso*quinoline derivative (IV) is obtained by the Bischler-Napieralski cyclisation of (III) with phosphorus pentoxide. It is significant to record that in the above conversion of (III : R = Me) to (IV : R = Me) (cf. Part V, *loc cit.*), carbon monoxide is now found* to be eliminated, as identified by a solution of sodium palladous chloride containing sodium acetate and confirmed by ammoniacal cuprous chloride adsorption. This lends an insight into the mechanism of the above reaction, and although the presence of ethanol could not possibly be detected in the reaction mixture, there is no doubt that the above reaction involves cyclodehydration and elimination of carbon monoxide and, consequently, of ethanol (cf. Mannich and Walther, *Arch. Pharm.*, 1927, **265**, 1 ; Rosenmund *et al.*, *Ber.*, 1927, **60**, 392). Work, which is now in progress to see if such elimination of carbon monoxide is taking place during the formation of fully aromatised *iso*quinoline derivatives, when α-methyl-α-acetamido-β-phenylpropionic acid or (α-acetamido-β-phenyl)-ethylmethyl ketone or their analogues are subjected to the Bischler-Napieralski cyclisation (cf. Ghosh and Dutta, this *Journal*, 1955, **32**, 17, 755 ; Ghosh, Bhattacharya and Dutta, *ibid.*, 1958, **35**, 758), will form the subject matter for a future communication.



*Jointly with B. K. Ghosh of this Institute.

EXPERIMENTAL

α-Amino-α-ethyl-β-phenylpropionic Acid (I: R = Et).—5-Benzyl-5-ethylhydantoin Herbst and Johnson, *J. Amer. Chem. Soc.*, 1932, **54**, 2463) (125 g.) was treated with aqueous NaOH solution (30%, 360 c.c.) and refluxed on a wiregauze for 24 hours. The solution was acidified with HCl and the unhydrolysed hydantoin filtered. The filtrate was evaporated to dryness on a steam-bath and the residue extracted with anhydrous ethanol. The ethanolic solution was concentrated and then treated with pyridine, when the amino-acid (23.5 g.) was precipitated. It was crystallised from aqueous ethanol as colorless microcrystalline powder, m.p. 282-83° (decomp.). (Found: N, 7.20. $C_{11}H_{15}O_2N$ requires N, 7.25%). It is readily soluble in aqueous sodium bicarbonate solution and in HCl (dilute).

α-Acetamido-α-ethyl-β-phenylpropionic Acid (II: R = Et).—The above amino-acid (6.72 g.) was mixed with acetic anhydride (5 g.) and pyridine (5 g.) and heated on a steam-bath for 5 hours. Pyridine was removed by steam distillation and the residual solid (7 g.) was crystallised from aqueous ethanol in colorless needles, m.p. 208-209°. (Found: N, 5.85. $C_{13}H_{17}O_3N$ requires N, 5.76%).

Ethyl α-Acetamido-α-ethyl-β-phenylpropionate (III: R = Et).—A mixture of (II: R = Et; 27 g.), ethanol (160 c.c.) and H_2SO_4 (conc., 1.6 c.c.) was heated under reflux on the steam bath for 8 hours. After distilling off the excess of ethanol under reduced pressure, the residue was poured into water and the mixture shaken with ether. The ether solution was washed with aqueous sodium bicarbonate solution and then with water and finally dried (sodium sulphate). Removal of the ether left a liquid which distilled at 164-65°/2-3 mm to a colorless heavy liquid (22 g.). (Found: N, 5.63. $C_{15}H_{21}O_3N$ requires N, 5.32%). On allowing it to stand, it solidified to furnish a colorless crystalline solid (m.p. 71-72°), which was readily soluble in ordinary organic solvents.

Action of P_2O_5 *on* (III: R = Et): *Formation of 1-Methyl-3-ethylisoquinoline* (IV: R = Et).—A mixture of the above ester (III: R = Et; 7 g.), P_2O_5 (28 g.) and anhydrous xylene (140 c.c.) was refluxed, under stirring, in an oil-bath for about 7 hours. Xylene was removed under reduced pressure and the residue treated with ice-water. The aqueous solution was washed with ether, treated with charcoal and filtered. The filtrate, on basification with caustic soda, furnished the base (4.2 g.), distilling at 118-19°/0.5-1 mm to a colorless liquid. (Found: N, 8.43. $C_{12}H_{13}N$ requires N, 8.19%).

The *picrate* was crystallised from ethanol (95%) in yellow needles, m.p. 178-79°. (Found: C, 54.31; H, 4.17; N, 14.31. $C_{12}H_{13}N.C_6H_3O_7N_3$ requires C, 54.0; H, 4.0; N, 14.0%).

Preparation of Benzylethyl Ketone (V: R = Et).—Ludlam (*J. Chem. Soc.*, 1942, **81**, 1189) had prepared this ketone by heating a mixture of calcium propionate and calcium phenylacetate. This method suffers from the main disadvantage in that the reaction mass consists of a mixture of benzylethyl, diethyl and dibenzyl ketones and it is naturally tedious to separate the first ketone in a pure form, the yield of which is rather poor. It has been, however, found advantageous to prepare benzylethyl ketone by hydrolysis of α-propionylphenylacetonitrile and subsequent decarboxylation. This nitrile has been prepared by Levine and Hauser (*J. Amer. Chem. Soc.*, 1946, **68**, 760)

by propionylation of phenylacetonitrile in presence of sodamide. We have, however, prepared this nitrile by adding rapidly a mixture of phenylacetonitrile (78.2 g.) and ethyl propionate (104.7 g.) to a warm solution of sodium (20.4 g.) in anhydrous ethanol (220 c.c.). After refluxing for about 7 hours, the reaction mixture was distilled under reduced pressure to remove ethanol. The residual mass was dissolved in a large volume of water, and the aqueous solution, after being washed with benzene, was acidified with acetic acid to furnish a colorless solid (85 g.), which could be crystallised from petroleum ether (b.p. 60-80°) in colorless needles, m.p. 72-73° (Levine and Hauser, *loc. cit.*, record m.p. 71-72.5°).

α-Propionylphenylacetonitrile (85 g.), thus prepared, was refluxed with a mixture of glacial acetic acid (170 c.c.) and HCl (conc., comml., 370 c.c.) for about 30 hours. The cooled mixture was extracted with benzene and the benzene solution was thrice washed with 10% NaOH solution and finally with water. Removal of benzene left a liquid (50 g.) which distilled at 226-27° (Ludlam, *loc. cit.*, records b.p. 227°). (Found C, 81 42 ; H, 8.32. Calc. for $C_{10}H_{12}O$: C, 81.08; H, 8.11%).

The *semicarbazone* was crystallised from ethanol in colorless needles, m.p. 152-53° (Ivanov, *Bull. Soc. Chim.*, 1937, *v*, **4**, 682, records m.p. 153°).

1-Phenyl-2-formamidobutane (VI: R=Et).—Formic acid (50 g., 98-100%) was neutralised with ammonium carbonate (50 g.) and the water was distilled from the solution till the temperature of the liquid recorded 165°. The solution was cooled to room temperature and benzylethyl ketone (27.8 g.) was added when a layer was formed. The flask was fitted with an upright air condenser which, in its turn, was connected to a downward condenser for distillation and a thermometer was fitted up to the bottom of the flask. The mixture was slowly heated to 180° when water distilled off and then heated at 180-85° for 8 hours. After cooling, the mixture was diluted with water and the oil was extracted with benzene ; the benzene solution was dried (sodium sulphate). Removal of benzene left a heavy dark liquid which distilled at 181-82°/2-3 mm to a straw-coloured heavy liquid (28.5 g.). (Found: N, 7.79. $C_{11}H_{13}ON$ requires N, 7.91%).

3-Ethyl-3 : 4-dihydroisoquinoline (VIII : R=Et).—In a flask, protected from moisture, were added P_2O_5 (111 g.) and orthophosphoric acid (85%, 72 c.c.) and the mixture was heated on a steam-bath for 2 hours under occasional shaking. To the cooled syrupy mass were added (VI : R=Et ; 17.5 g.) and $POCl_3$ (22.5 c.c.) and the reaction mixture was heated at 125-30° for 8 hours. The mass was cooled, treated with ice-water and washed with ether. The aqueous solution, on basification with NaOH, liberated the base, which was extracted with ether. Removal of the ether left a mobile red liquid (12 g.) which distilled at 107-108°/1-2mm to a colorless liquid.

The *picrate* was crystallised from ethanol in yellow needles, m.p. 130-31°. (Found : N, 14 67. $C_{11}H_{13}N.C_6H_3O_7N_3$ requires N, 14.43%).

3-Ethylisoquinoline (IX: R=Et).—A mixture of (VIII : R = Et ; 8 g.), tetralin (36 c.c.) and Pd—C (10%, 2.4 g.) was heated at 240-45° for 4 hours in an atmosphere of CO_2. The mixture was filtered and washed with ether. From the filtrate the base was isolated by extraction with HCl (dilute). The acid solution, on basification with NaOH, furnished the base (6.5 g.) which distilled at 112-13°/1 mm to a colorless liquid.

The *picrate* was crystallised from a large quantity of ethanol in yellow plates, m.p. 174-75° (Damerow, *loc. cit.*, records m. p. 171-72°). (Found: N, 14.62. Calc. for $C_{11}H_{11}N.C_6H_3O_7N_3$: N, 14.51%).

1-Phenyl-2-aminobutane (VII: R=Et).—A mixture of (VI: R=Et: 33.5 g.) and HCl (conc., 22.5 c.c.) was refluxed for 8 hours when it turned dark in colour. The mixture was poured into ice-water and washed with benzene. The aqueous solution, when basified with NaOH, furnished the base which was extracted with benzene. Removal of benzene left a liquid (22.5 g.) which distilled at 117-18°/20-21 mm to a colorless liquid (Kornblum and Iffland, *loc. cit.*, record b.p. 106°/15 mm). (Found: N, 9.39. Calc. for $C_{10}H_{15}N$: N, 9.39%).

The *picrate* was obtained in benzene solution as yellow plates, m.p. 130-31°. (Found: N, 14.58. $C_{10}H_{15}N.C_6H_3O_7N_3$ requires N, 14.81%).

The *benzoyl* derivative was crystallised from aqueous ethanol in colorless needles, m.p. 124-25° (Kornblum and Iffland, *loc. cit.*, record m.p. 122-22.5°).

1-Phenyl-2-acetamidobutane (X: R=Et).—A mixture of (VII: R=Et; 20.76 g.), acetic anhydride (20 g.) and pyridine (20 g.) was heated on the steam-bath for 5 hours. Pyridine was removed by steam distillation and the residual oil (25 g.), on keeping, gradually solidified. It was crystallised from petroleum ether (b.p. 60-80°) in colorless needles, m.p. 69-70°. (Found: N, 7.08. $C_{12}H_{17}ON$ requires N, 7.33%).

1-Methyl-3-ethyl-3:4-dihydroisoquinoline (XI: R=Et).—A mixture of (X: R=Et; 10 g.), $POCl_3$ (10 g.) and benzene (100 c.c.) was refluxed for 8 hours, cooled and then poured into ice-water under shaking. The aqueous layer was separated and basified with NaOH. The liberated base was extracted with ether, and removal of the ether left a liquid (5 g.) distilling at 115-16°/1-2 mm to a colorless liquid. (Found: N, 8.34. $C_{12}H_{15}N$ requires N, 8.09%).

The *picrate* was crystallised from ethanol in yellow needles, m.p. 167-68°. (Found: N, 13 68. $C_{12}H_{15}N.C_6H_3O_7N_3$ requires N, 13.93%).

Dehydrogenation of the above base over Pd−C (10%) in presence of tetralin, according to the process described earlier, furnished a base, the picrate of which was found identical with that of (IV: R=Et), as confirmed by mixed m.p. and elemental analysis.

5-Benzyl-5-propylhydantoin.—A mixture of benzylpropyl ketone (Ishiwata and Suzuki, *loc. cit.*, 15.5 g.), ammonium carbonate (44.7 g.), potassium cyanide (12.5 g.), ethanol (89.4 c c.) and water (89.4 c.c.) was heated at 50-60° for 8 hours and then at 70-80° for another 8 hours. The mixture was concentrated and then acidified with HCl. The solid (21.6 g.) was crystallised from ethanol in colorless prisms, m.p. 206-207°. (Found: N, 12.29. $C_{13}H_{16}O_2N_2$ requires N, 12.07%).

α-Amino-α-propyl-β-phenylpropionic acid (I: R=Pr) was prepared from the above hydantoin as in the case of (I: R=Et) and was crystallised from aqueous ethanol in colorless clusters of needles m. p. 285-86° (decomp.). (Found: N, 6.48. $C_{12}H_{17}O_2N$ requires N, 6.76%).

α-Acetamido-α-propyl-β-phenylpropionic acid (II: R=Pr) was prepared in the usual way and was crystallised from ethanol in colorless needles, m.p. 223-24°. (Found: N, 5.84. $C_{14}H_{19}O_3N$ requires N, 5.62%).

Ethyl α-acetamido-α-propyl-β phenylpropionate (III : R = Pr) was prepared in the usual way and distilled at 175-76°/4-5 mm to a thick colorless liquid. (Found : N, 4.68. $C_{16}H_{23}O_3N$ requires N, 5.05%). On keeping it solidified to furnish a colorless crystalline solid (m.p. 63-64°), readily soluble in ordinary organic solvents.

Action of P_2O_5 *on* (III : R = Pr) : *Formation of 1-Methyl-3-propylisoquinoline* (IV : R = Pr).—The method of procedure was the same as in the case of (III : R = Et). The base distilled at 120-21°/0.5 mm to a colorless liquid and was characterised as *picrate*, crystallising from ethanol in yellow prisms, m.p. 144-45°. (Found : N, 13.68. $C_{12}H_{15}N.C_6H_3O_7N_3$ requires N, 13.53%).

1-Phenyl-2-formamidopentane (VI : R = Pr) was similarly prepared, as in the case of (VI : R = Et), by the action of ammonium formate on benzylpropyl ketone (Ishiwata and Suzuki, *loc. cit.*) and distilled at 178-79°/4-5 mm to a colorless heavy liquid. (Found : N, 7.17. $C_{12}H_{17}ON$ requires N, 7.33%).

3-Propyl-3 : 4-dihydroisoquinoline (VIII : R = Pr) was prepared from (VI : R = Pr) by the action of $POCl_3$ and polyphosphoric acid, according to the process described previously, and distilled at 120-21°/4-5 mm. The *picrate* was crystallised from ethanol in yellow needles, m.p. 120-21°. (Found : N, 14.12. $C_{12}H_{15}N.C_6H_3O_7N_3$ requires N, 13.93%).

3-Propylisoquinoline (IX : R = Pr) was prepared from (VIII : R = Pr) by dehydrogenation over Pd−C (10%) in tetralin, according to the process described previously, and was characterised as picrate, crystallising from ethanol in yellow needles, m.p. 163-64° (Albahary, *loc. cit.*, records m.p. 161°). (Found : N, 14.21. Calc. for $C_{12}H_{13}N.C_6H_3O_7N_3$: N, 14.0%).

1-Phenyl-2-aminopentane (VII : R = Pr) was obtained from (VI : R = Pr) by hydrolysis with HCl (conc.) in the usual way and distilled at 104-105°/5-6 mm (Kornblum and Iffland, *loc. cit.*, record b. p. 118°/15 mm). (Found : N, 8.89. Calc. for $C_{11}H_{17}N$: N, 8.59%).

The *benzoyl* derivative was crystallised from ethanol in colorless rectangular plates, m.p. 124-25° (Kornblum and Iffland, *loc. cit.*, record m.p. 123-123.5° ; Ishiwata and Suzuki, *loc. cit.*, record m.p. 120°).

1-Phenyl-2-acetamidopentane (X : R = Pr) was prepared from (VII : R = Pr) in the usual way and was crystallised from ethanol in colorless needles, m.p. 91-92°. (Found : N, 6.55. $C_{13}H_{19}ON$ requires N, 6.83%).

1-Methyl-3-propyl-3 : 4-dihydroisoquinoline (XI : R = Pr) was obtained from (X : R = Pr) by treatment with $POCl_3$ in presence of benzene in the usual way and distilled at 103-104°/1-2 mm to a colorless liquid.

The *picrate* was crystallised from ethanol in yellow needles, m.p. 152-53°. (Found : N, 13.56. $C_{13}H_{17}N.C_6H_3O_7N_3$ requires N, 13.46%).

Dehydrogenation, in the usual way, of the above base over Pd−C (10%) in presence of tetralin has furnished a base, the picrate of which has been found to be identical with that of (IV : R = Pr), as confirmed by mixed m.p. and elemental analysis.

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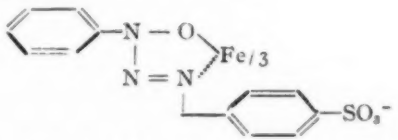
SPECTROPHOTOMETRIC AND CONDUCTOMETRIC STUDIES OF METAL COMPLEXES OF 3-HYDROXY-1-*p*-SULPHONATOPHENYL-3-PHENYLTRIAZINE. PART IV. IRON COMPLEX

By R. N. Mathur and N. C. Sogani

Fe^{III} forms a bluish black, water-soluble complex with 3-hydroxy-1-*p*-sulphonatophenyl-3-phenyltriazine. The formula of the complex, established spectrophotometrically by applying Job's continued variation method, slope ratio method and molar ratio method, has been found to be FeR_3 (R = reagent) in the *p*H range between 2.0 and 4.3. At higher *p*H values FeR^{2+} and FeR_2^+ are indicated. Conductometrically all the three formulae are indicated. The dissociation constant of FeR_3 at 20° is 2.38×10^{-13} and the free energy of formation of the complex is −15.59 K cal./mole.

3-Hydroxy-1-*p*-sulphonatophenyl-3-phenyltriazine has been used for the spectrophotometric determination of iron (Gupta and Sogani, this *issue*, p. 97). From the absorption curves of iron complexes at different *p*H values and also from the effect of *p*H on absorbance (*loc. cit.*), iron complexes of different compositions at different H^+-ion concentrations are indicated.

The present investigation was undertaken with a view to establishing the formulae of iron—3-hydroxy-1-*p*-sulphonatophenyl-3-phenyltriazine complexes at different *p*H values, using spectrophotometric and conductometric methods. The empirical formula, in the *p*H range between 2.0 and 4.3, has been found to be FeR_3. The chelate structure may be represented as:



Job's continued variation method (*Ann. chim.*, 1928, *x*, **9**, 113) has been applied to study the formulae of iron complexes at higher *p*H values. At *p*H 5.5, the empirical formulae have been found to be FeR_1 and FeR_2 at 520 mμ and FeR_2 at 650 mμ. There is no indication of FeR_3 at this H^+-ion concentration. Conductometrically all the above three formulae are indicated.

The dissociation constant and, hence the stability constant, and the free energy of formation of iron complex, FeR_3, have been determined.

Experimental

Standard ferric chloride solution, prepared as described (*loc. cit.*), was diluted to provide $M \times 10^{-3}$ for conductometric work and Job's method, and $M \times 10^{-4}$ and $M \times 10^{-5}$ for slope ratio method (Harve and Manning, *J. Amer. Chem. Soc.*, 1950, **72**, 4488). Reagent solution, buffer solutions, instruments, etc. were the same as described in Part I (this *Journal*, 1958, **35**, 542).

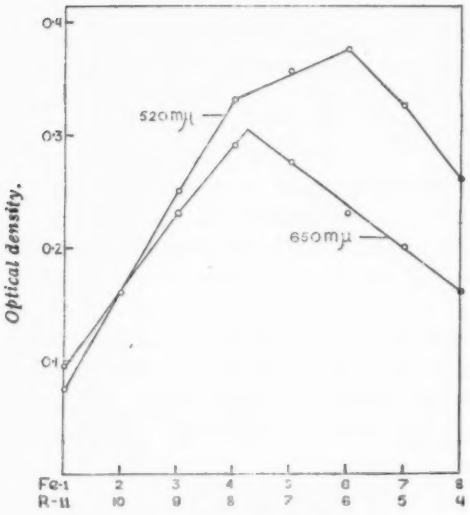
Nature of the Complex Formed.—The absorption spectra of mixtures of equimolar solutions of ferric chloride and the reagent, in the ratios of 1 : 1, 1 : 2, 1 : 3, etc., at *p*H 2.5 and 5.5 were studied. The curves at *p*H 2.5 were different than those at *p*H 5.5 (Fig. 1, *loc. cit.*), thus indicating the formation of different complexes at different *p*H values (Vosburgh and Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437).

Composition of the Complex

The molar compositions of iron complexes were investigated by the following methods.

Job's Method.—A series of solutions was prepared from $M \times 10^{-3}$ solutions of the metal and the reagent in which the ratios of iron to reagent varied from 1 : 11 to 11 : 1. In one set of experiments the *p*H was kept at about 2.5 and in the other set, at *p*H 5.5. Absorbance of the mixtures were measured at 520 and 650 mμ. At *p*H 2.5 the maxima at 3 : 9 ratio of iron to reagent at both the wavelengths indicated FeR_3 as the formula of the complex. Fig. 1 shows the curves obtained at *p*H 5.5. At 520 mμ the breaks in the curve at 4 : 8 and 6 : 6 ratios of iron to reagent indicate FeR_2 and FeR_1 as the formulae of the complexes. At 650 mμ, only FeR_2 is indicated. However, at higher *p*H there is no indication of FeR_3.

FIG. 1

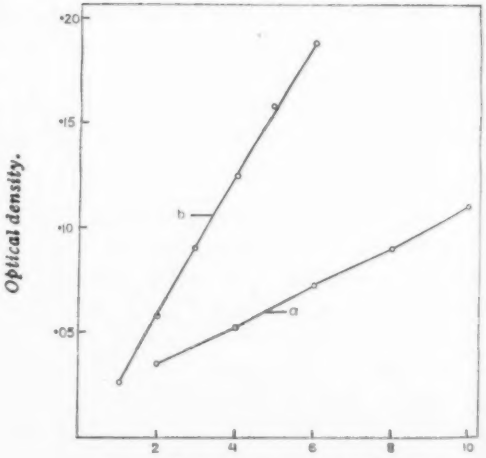


*p*H = 5.5 5.6. R = Reagent.

Slope Ratio Method.—There was some difficulty in applying this method for determining the formula of the iron complex. Though the colour formation was instantaneous, yet the solutions containing excess iron faded within 10 minutes. However, in case of excess of the reagent, the complex was fairly stable. The fading of the colour in the former case probably is due to the oxidising action of excess of ferric ions on the very low concentrations of the reagent. Because of this reason, the absorbance of different solutions was measured immediately after these were prepared. The concentration of the variable component was varied from 1×10^{-5} to $10 \times 10^{-5} M$ in the excess concentration of $8 \times 10^{-4} M$ of the constant component. The *p*H of the solutions was kept at about 2.5. Fig. 2 records the measured optical density at 650 mμ, plotted against the concen-

FIG. 2

*p*H 2.5 650mμ.

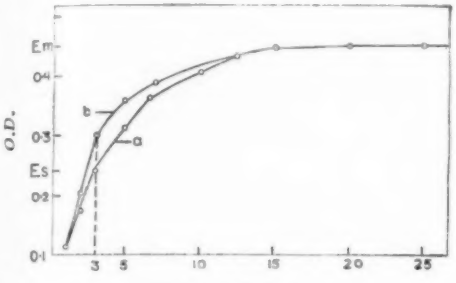


Conc. of variable component ($M \times 10^5$).
a : reagent varying. b : Fe varying.

tration of the variable component. The slopes of the two straight lines afford iron to reagent ratio as 1 : 3.

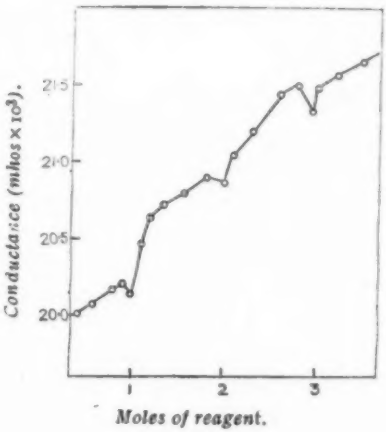
Molar Ratio Method (Yoe and Jones, *Ind. Eng. Chem., Anal Ed.*, 1944, **16**, 111).—Varying amounts of $2 \times 10^{-3}M$ reagent solution were added to a series of solutions containing 5 c.c. of $10^{-3}M$ iron. *p*H was adjusted to about 2.5. There is a slight break in the curve 'a' (Fig. 3) at a ratio of 3 moles of the reagent to 1 mole of iron, suggesting the formula of the complex as FeR_3. By repeating the above experiment in presence of 5 c.c. of *M*-KCl a better break in the curve is obtained (curve 'b').

FIG. 3



Conductivity Method.—$M \times 10^{-3}$-ferric chloride (10 c.c., *p*H 2.5) solution was taken in a conductivity cell and its conductance was measured; $5 \times 10^{-3}M$-reagent solution (*p*H 2.5, adjusted with HCl) was added from a burette. The observed conductance was corrected for volume. Fig. 4 shows the conductance values plotted against moles of the reagent added. The formation of three complexes: FeR^{2+}, FeR_2^{+} and FeR_3 is indicated during the course of the reaction.

FIG. 4



The reaction takes place in three steps. The equations may be written as:

$$Fe^{3+} + RH \rightleftharpoons FeR^{2+} + H^{+} \quad \ldots (1)$$

$$FeR^{2+} + RH \rightleftharpoons FeR_2^{+} + H^{+} \quad \ldots (2)$$

$$FeR_2^{+} + RH \rightleftharpoons FeR_3 + H^{+} \quad \ldots (3)$$

Consider the first step (equation 1). During the course of reaction Fe^{3+} ions are replaced by less mobile FeR^{2+} complex ions and more mobile H^{+} ions. The former decreases the conductance whereas the latter increases it. The latter effect more than compensates the decrease in conductance due to the former effect. The curve therefore shows a continuous increase in conductance. At the equivalence point there is a sudden disappearance of all Fe^{3+} and the conductance is due to only H^{+} ions and FeR^{2+} ions; hence, there is a slight fall in the conductance. This indicates the formula of the complex.

DISCUSSION

The dissociation of the complex may be written as:

$FeR_3 \rightleftharpoons$	Fe^{3+} +	$3R^-$	
C	0	0	Initial conc.
$(1-\alpha)C$	αC	αC	Final conc.

where C is the concentration of the complex, assuming no dissociation, and α is the degree of dissociation. The dissociation constant, K, is given by the equation

$$K = \frac{C \times (3\ \alpha C)^3}{C(1-\alpha)} = \frac{27\ \alpha^4 C^3}{1-\alpha}.$$

From curve 'a'. Fig. 3

$$\alpha = \frac{E_m - E_s}{E_m} = \frac{0.45 - 0.24}{0.45} = 0.466$$

(where the terms have their usual significance). The concentration C of the complex is equal to the total concentration of iron, which is $10^{-4}M$.

By substituting these values in the above equation, the value of K at 20° comes to 2.38×10^{-12}. Hence, the stability constant K' is equal to 4.2×10^{11}.

The standard free energy of formation of the complex from ferric chloride and 3-hydroxy-1-*p*-sulphonatophenyl-3-phenyltriazine is calculated from the relation $\Delta F^\circ = RT \ln K$ and works out to -15.59 K cal./mole at 20°.

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BIOCHEMICAL CHANGES IN BACTERIA IRRADIATED WITH ULTRAVIOLET LIGHT

By A. Mukherji and Miss J. Chatterji

Ultraviolet irradiation in sublethal dose of certain gram-negative micro-organisms has been found to cause considerable alteration of their biochemical characters. Methyl red reaction and indole formation increase generally; irradiated *Shigella sonnei* and *Pseudomonas pyocyaneus* form indole; citrate utilisation, Voges-Proskauer reaction and nitrate reduction decrease. In most of the organisms fermentation characters regarding sugars and alcohols are altered.

Works on the effects of irradiation on micro-organisms were in the past largely directed to the study of lethal effect. More recently (Lewis, *J. Bact.*, 1934, **28**, 616; Stewart, *J. Hyg.*, 1942, **41**, 497) ultraviolet and other irradiations have been used for bacterial mutations. Mukherji (*Ind. J. Med. Res.*, 1952, **40**, 167) has shown that smears of gram-negative bacteria on irradiation for two hours change to gram-positive. The present work deals with biochemical changes in bacteria effected by irradiation with UV light.

Experimental

Light as emitted from a portable Hanovia UV lamp with a deep violet filter was used in this work. The wave-lengths of the light emitted lie between 2000 and 3000Å. The light caused erythema of the skin with a subject of light wheat colour, when exposed for a minimum of nine minutes at a distance of one metre.

The various bacteria used in this work were grown in ordinary nutrient broth of *p*H 7.2 for 18 hours at 37° and a few drops from these cultures were introduced in quartz tubes containing the same quality of nutrient broth so as to contain about 250 million organisms per cm^3. The quartz tubes were obtained from Heraus Quartzschmelze, Hanau, Germany. The external diameter is approximately 8.5 mm and the internal diameter, 7 mm. After inoculation the quartz tubes were kept at a mean temperature of 35° and exposed to the UV light from the Hanovia lamp at a distance of one metre from the bulb for a period of 3 hours with occasional shaking. The shaking was done with a view to effecting as uniform an exposure of the culture mass as possible to the radiation of the UV light. A set of ten sugar tubes containing 1% each of different sugars in ordinary nutrient broth with Andrade's indicator and media for the testing of methyl red, the Voges-Proskauer's reaction, indole formation, citrate utilisation and nitrate reduction were inoculated with one drop each of the irradiated cultures. Control tests with each of the cultures, which were grown in nutrient broth for 3 hours at 35° (but not irradiated), were also put up simultaneously. The inoculated tubes for the Voges-Proskauer test were incubated at 30° and others at 37°

for 5 days. This was found necessary since the *Aerobacter aerogenes* used in this work is V.P. positive only, when incubated at this temperature. In the case of the Voges-Proskauer, methyl red and ether tests, 3 drops of culture were inoculated in 3 c.c. of the medium. Opacity of the various culture tubes including sugars was found to be almost the same in 24 hours in irradiated and control cultures.

TABLE I

Biochemical reactions.

Bacteria.	Methyl red.		Citrate utilisation.		Indole formation.		Nitrate reduction.	
	Irrad.	Contr.	Irrad.	Contr.	Irrad.	Contr.	Irrad.	Contr.
S. paratyphi	+++	++	+	++	−	−	Trace	+
S. schottmuleri	+++	++	+	++	−	−	Trace	+
S. typhi	+++	++	+	++	−	−	Trace	+
E. coli	++++	++	++	+++	+++	++	+	++
A. aerogenes	−	−	++	+++	+++	+	Trace	++
P. pyocyaneus	−	Trace	++	+++	+++	+,−	Trace	+
Sh. dysenteriae	++	+	−	−	−	−	Trace	+
Sh. paradysenteriae	++	+	−	−	++	−	−	−
Sh. sonnei	++	+	−	Trace	++	−	−	−
B. subtilis	++	+	+++	++++	−	−	Trace	+

N.B. +,++,+++,++++ indicate the reaction to be just positive, moderately positive, strongly positive and very strongly positive, respectively; − denotes negative.

TABLE II

Fermentation of sugars and alcohols.

Bacteria.	Glucose.		Lactose.		Mannite.		Mannose.		Maltose.	
	Irr.	Contr.	Irr.	Contr.	Irr.	Contr.	Irr.	Contr.	Irr.	Contr.
S. paratyphi	+	+	⊥	±	+ ⊥	+	+ ⊥	+	⊥ +	+
S. schottmuleri	+	+	−	−	+	−	+	+	+ ⊥	+
S. typhi	⊥	⊥	⊥ ±	⊥	⊥	⊥	⊥	⊥	⊥ +	⊥
E. coli	+	+	±	+	+	+	+	+	+	+
A. aerogenes	+	+	+	+	+	+	−	−	⊥ +	+
P. pyocy neus	⊥	⊥	−	−	−	−	−	−	−	−
Sh. dysenteriae	⊥	⊥	⊥	−	−	−	⊥	−	⊥	−
Sh. paradysenteriae	⊥	⊥	⊥	−	⊥ +	⊥	⊥	−	⊥	⊥
Sh. sonnei	⊥	⊥	⊥	⊥	⊥	⊥	⊥	⊥	⊥	⊥
B. subtilis	⊥	⊥	⊥	−	−	⊥	⊥	⊥	⊥	⊥

N.B. + denotes acid and gas; ⊥ denotes gas and − denotes no reaction

TABLE III

Fermentation of sugars and alcohols.

Bacteria.	Arbinose.		Dulcitol.		Sorbitol.		Sucrose.		Xylose.	
	Irr.	Contr.	Irr.	Contr.	Irr.	Contr.	Irr.	Contr.	Irr.	Co..tr.
S. paratyphi	+ ⊥	+	+ ⊥	+	⊥	+	−	−	⊥	−
S. schottmuleri	⊥	+	+	+	+	+	−	−	+ ⊥	+
S. typhi	⊥ ±	−	⊥	−	⊥	⊥	±	−	⊥	⊥
E. coli	±	+	+	+	+	+	−	−	+	+
A. aergoenes	+	+	−	−	+	+	+	+	⊥ +	+
P. pyocyaneus	⊥	−	⊥	−	⊥	−	⊥	−	⊥	⊥
Sh. dysenteriae	⊥	−	−	−	⊥	⊥	−	−	⊥	−
Sh. paradysenteriae	⊥	−	−	−	−	−	⊥	−	⊥	−
Sh. sonnei	−	⊥	−	−	⊥	−	−	⊥	−	⊥
B. subtilis	−	⊥	−	−	−	⊥	− ⊥	⊥	⊥	⊥

N.B. Symbols have the same significance as in Table II.

DISCUSSION

It will be observed that irradiation with ultraviolet light brings about certain changes in the living bacteria. That the bacteria remain alive after three hours' irradiation has been very carefully tested. Besides the fact that the bacteria are capable of fermenting sugars and alcohols and bring about other biochemical changes, growth is also evident from the opacity of the media inoculated. The irradiated bacteria were subcultured in sugar media for two more generations in the case of *P. pyocyaneus* and *Sh. sonnei*. Fermentation of sugars did take place as with the first generation of the irradiated culture. These irradiated *E. coli* and *S. typhi*, when grown with phage isolated from local patients, supported the growth of the phage. Therefore the unavoidable conclusion is that the bacteria after irradiation remain viable.

Methyl red reaction is substantially increased with all the irradiated bacteria, excepting in the cases of *A. aerogenes* and *P. pyocyaneus*, which are normally negative. Further, indole formation is not only increased with irradiated *E. coli*, *A. aerogenes*, *Shigella paradysenteriae* Flexner, but *Sh. sonnei* and *P. pyocyaneus*, which do not normally form indole, begin to produce this substance after irradiation with ultraviolet light. On the other hand, ultraviolet irradiation considerably decreases the Voges-Proskauer reaction with *A. aerogenes*, and citrate utilisation and nitrate reduction with *S. paratyphi*, *S. schottmuelleri*, *S. typhi*, *E. coli* (this particular strain utilised citrate for its growth), *A. aerogenes*, *P. pyocyaneus* and *B. subtilis*. Nitrate reduction with irradiated *Sh. dysenteriae*, Shiga was also inhibited.

Fermentations of various sugars and alcohols have been found to be constant with irradiated *Sh. sonnei* anh *P. pyocyaneus*. With other irradiated bacteria, while certain types of fermentations were nearly constant, occasionally there were partial or complete inhibition of a particular fermentation or even a change from only acid production to one of acid and gas.

Irradiated *P. pyocyaneus* and *Sh. sonnei* produced more or less the same type of sugar fermentations in all the three generations. The detailed genetic study is being undertaken for a subsequent communication. No special explanation for the changed biochemical properties are being attempted in this paper beyond stating the relevant work of Spiegel-Adolf (*Med. Rec.*, 1939, **150**, 430) that ultraviolet light brings about an alteration in the proteins and therefore also of the enzymes.

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SILVER-CATALYSED REDUCTION OF PERSULPHATE BY FORMIC ACID

By V. K. Gupta and R. K. Nigam

Silver-catalysed reduction of persulphate by formic acid has been studied by following the kinetics iodometrically. The reaction is of first order in persulphate and independent of the concentration of formic acid. Salt-effect could not be determined owing to the specific influence of the ions. Nitrate ion greatly inhibits the reaction. Frequency factor has been calculated and a mechanism suggested. A white turbidity is obtained if sodium or potassium formate is employed in place of formic acid.

Uncatalysed reduction of persulphate by sodium formate (*Z. physikal. Chem.*, 1953, **202**, 198) and formic acid (unpublished) has been studied by Srivastava and Ghosh. Silver ion was reported to be a good catalyst, but no systematic and detailed study was made by them. We have carried out the investigations with potassium and sodium formates and found the first order constants to decrease with time during any run, and a white turbidity to appear in the reaction mixture, which ultimately turned grey. This occurred as a result of the reduction of silver nitrate by formate. However, there appeared little or no turbidity on employing formic acid in presence of sulphuric acid, the concentration of silver ion being kept low. The kinetics were followed by estimating the persulphate iodometrically by the method of Szabo *et al.* (*Z. anal. Chem*, 1952, **135**, 269).

A preliminary study indicated that the persulphate reacted only very slowly with the formate or formic acid in absence of silver. The course of reaction was followed by two methods. In one of them, using formate, the acid obtained by the reduction of persulphate was estimated by a standard alkali and in the other, using both formate and formic acid, persulphate was estimated iodometrically (*loc.cit.*). We failed to observe any reaction within 40 minutes at 35° by the second method, whereas by the first method, only approximately 1/20 persulphate reacted in the same period. Also, we tried to study the silver-catalysed reaction by estimating the acid, but no regular and reproducible results were obtained. It appears that the method of estimating the acid is not free from objection.

Experimental

All the chemicals used were of B. D. H.-A. R. or E. Merck-G.R. quality. All the vessels and the apparatus used in this investigation were of Jena glass and the medium of reaction was redistilled water from a pyrex vessel. Stock solutions of formic acid and silver nitrate were prepared in redistilled water and the acid was standardised by NaOH.

Persulphate solution was always freshly prepared by direct weighing and its concentration checked by Eckardt's method (*Chem. News*, 1900, **81**, 38).

The reaction was studied at 35° in a thermostat. Silver nitrate was added in the end to start the reaction. The total volume of the reaction mixture was 100 c.c. The reaction mixture (5 c.c.) was taken out at suitable intervals of time and added to a beaker containing 2.5 c.c. of 60% KI, 10 c.c. of HCl (~ 3*N*) and 1 c.c. of the catalyst. The catalyst was prepared by dissolving 2.59 g. of A. R. ferrous ammonium sulphate and 9.82 g. of A.R. copper sulphate in 500 c.c. of distilled water HCl checked the reaction by precipitating silver as chloride, and unchanged persulphate and copper sulphate liberated iodine. Moreover, the chloride ions inhibited the uncatalysed reaction, as reported by Srivastava and Ghosh (*loc.cit.*). The iodine was titrated against 0.04*N* sodium thiosulphate from a microburette. A blank was also run with the catalyst and all other reactants, excepting the persulphate and the blank, were subtracted from the reading of the microburette. There was no significant reaction between liberated iodine and formic acid within the time for which the titration was performed.

Discussion

The first order constants were calculated from the relation :

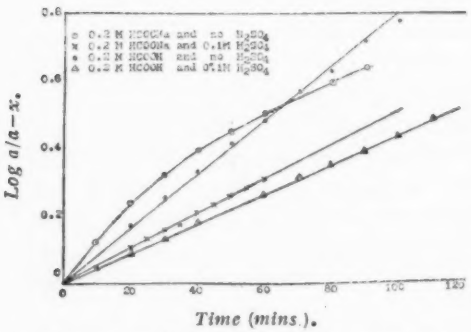
$$k = (2.303/t) \times (1/C_{Ag^+}) \times (\log a/a-x) \quad \ldots \quad \ldots \quad (1)$$

where 'a' and '$a-x$' are the concentrations of persulphate initially and after time 't', and C_{Ag^+} is the concentration of the catalyst.

Some of the results are shown in Fig. 1 where log $a/a-x$ has been plotted against time. No straight line is obtained in case of sodium formate. The first order constants decrease with time, as mentioned earlier. Gradual decrease of concentration of the catalyst by reduction may be one reason for this. Another reason may be the progressive formation of sulphuric acid in the reaction mixture, which slows down the reaction. This may easily be concluded from the other curves where straight lines are obtained and where the slope of these lines is less than that in the case of sodium formate. We have therefore employed formic acid in place of sodium formate, and also sulphuric acid to minimise the chances of reduction of silver nitrate by formic acid. Higher concentrations of silver nitrate and formic acid could not be used for the same reason.

FIG. 1

$K_2S_2O_8 = 0.02M$. $AgNO_3 = 0.001M$.



Further results employing formic acid with sulphuric acid are recorded in Tables I and II, which show the effect of using different concentrations of the reactants.

TABLE I

$HCOOH = 0.2M$. $H_2SO_4 = 0.1M$. $AgNO_3 = 0.001M$.

Time.	0.02M-$K_2S_2O_8$. $Na_2S_2O_3$.	k.	0.03M-$K_2S_2O_8$. $Na_2S_2O_3$.	k.	0.04M-$K_2S_2O_8$. $Na_2S_2O_3$.	k.
0 min.	4.98 c.c.	...	7.51 c.c.	...	10.04 c.c.	..
10	4.40	12.37	...	...	8.90	12.04
20	4.06	10.21	6.00	11.21	8.02	11.23
30	3.66	10.27	5.44	10.74	7.28	10.72
40	3.30	10.29	4.88	10.77	6.58	10.56
50	...	...	4.38	10.78	5.98	10.36
60	2.70	10.14	3.96	10.68	5.38	10.40
70	2.44	10.19	3.54	10.74	4.80	10.54
80	2.20	10.21	3.20	10.67	4.46	10.15
90	2.00	10.14	2.94	10.42	4.04	10.12
100	1.80	10.17	2.66	10.48	3.60	10.27
110	1.62	10.21	2.34	10.60	3.28	10.17
120	1.48	10.11	2.12	10.55	2.98	10.13
Average		10.20		10.64		10.34

TABLE II

$K_2S_2O_8 = 0.02M$. $H_2SO_4 = 0.1M$. $AgNO_3 = 0.001M$.

Time.	0.2M-HCOOH. $Na_2S_2O_3$.	k.	0.1M-HCOOH. $Na_2S_2O_3$.	k.	0.05M-HCOOH. $Na_2S_2O_3$.	k.	0.02M-HCOOH. $Na_2S_2O_3$.	k.	0.01M-HCOOH. $Na_2S_2O_3$.	k.
0 min.	4.98 c.c.	...	5.20 c.c.	...	5.02 c.c.	...	5.02 c.c.	...	5.02 c.c.	...
10	4.40	12.37	...	...	4.44	12.27	4.56	10.39	4.56	10.39
20	4.06	10.21	4.04	12.62	3.98	10.86	...	...	4.30	9.74
30	3.66	10.27	3.60	10.18	3.64	10.72	3.84	8.93	3.98	7.74
40	3.30	10.29	3.26	10.03	3.36	10.04	3.54	8.73	3.70	7.63
50	...	...	2.98	10.43	3.04	10.03	3.26	8.64	...	...
60	2.70	10.14	2.72	10.20	2.74	10.09	3.00	8.58	3.20	7.51
70	2.44	10.19	2.52	10.35	2.50	9.96	2.76	8.54	2.98	7.45
80	2.20	10.21	2.24	10.08	2.28	9.86	2.56	8.36	2.80	7.29
90	2.00	10.14	2.04	10.43	...	...	2.38	8.29	2.62	7.23
100	1.80	10.17	1.88	10.15	1.84	10.04	2.22	8.16	2.46	7.13
110	1.62	10.21	1.64	10.17	1.68	9.95	...	...	...	...
120	1.48	10.11	1.48	10.18	1.54	9.85	...	...	...	...
Average		10.20		10.22		10.11				

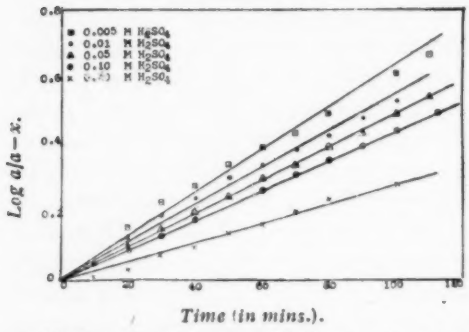
The reaction is thus first order in persulphate and independent of the concentration of formic acid, when in excess. With lower concentrations of formic acid, the rate constants decrease with time during the run. It appears from this that there is a step of reaction which ordinarily is fast, but becomes slow when the concentration of formic acid is low. This will be dealt with in more detaiis when the mechanism is discussed.

The rate also depends on the concentration of silver nitrate. The rate constants were 0.00523 and 0.00266 for 0.0005M and 0.00025M concentrations of silver nitrate respectively. These constants on division by the respective concentrations of silver nitrate yield the values 10.46 and 10.66 in agreement with relation (1).

Effect of Varying the Concentration of H_2SO_4.—Fig. 2 shows the results in presence of varying amounts of H_2SO_4. The velocity constants decrease as the concentration of the acid is increased in different experiments. At lower concentrations of the acid, the constants decrease with time during any run. This further confirms that H_2SO_4 is gradually produced which increases the total concentration of the acid, causing progressive inhibiting action in the reaction. At higher concentrations of H_2SO_4, formation of the acid does not substantially increase the concentration and, hence, fairly uniform constants are obtained. It is difficult to understand the role of sulphuric acid in persulphate oxidations. It retards the rate in the silver catalysed oxidation of oxalic acid (Gupta and Ghosh, *Proc. Nat. Acad. Sci.*, 1958, **27A**, 258) and hydrogen peroxide (Srivastava and Ghosh, *ibid.*, 1954, **23A**, 44) as in the present case. On the other hand, it increases the rate in the catalysed oxidation of potassium oxalate (Gupta and Ghosh, *J. Inorg. Nucl. Chem.*, 1959, **9**, 178) and uncatalysed oxidation of oxalic acid (Srivastava and Ghosh, *Z. physikal. Chem.*, 1956, **205**, 332). In the catalysed oxidation of arsenious acid (Gupta and Misra, unpublished), it has an optimum concentration for which the reaction is fastest, whereas in the uncatalysed oxidation (Gupta, this *Journal*, 1959, **36**, 643) the acid has an irregular behaviour. This points to the fact that the mechanism of the reaction is not exactly similar in all these cases.

FIG. 2

$K_2S_2O_8 = 0.02M$. $AgNO_3 = 0.001M$.



Specific Effect of the Ions.—Several electrolytes were employed to note the salt-effect, but it could not be determined owing to the specific influence of the ions as in other persulphate oxidation reactions. Table III records the velocity constants in presence of these electrolytes.

TABLE III

$K_2S_2O_8 = 0.02M$. $HCOOH = 0.2M$. $H_2SO_4 = 0.1M$. $AgNO_3 = 0.001M$.

Electrolyte.	Conc.	k.
...	...	10.20
K_2SO_4	0.250 *M*	6.05
K_2SO_4	0.125	6.25
K_2SO_4	0.050	8.81
$MgSO_4$	0.500	7.44
$MgSO_4$	0.250	7.64
$MgSO_4$	0.050	8.08
$(NH_4)_2SO_4$	0.250	9.13
$(NH_4)_2SO_4$	0.125	9.75

TABLE IV

Conditions are the same as in Table III.

Electrolyte.	Conc.	k.
...	...	10.20
KNO_3	0.250 *M*	1.96
KNO_3	0.125	2.76
NH_4NO_3	0.250	2.58
NH_4NO_3	0.125	3.61
$NaNO_3$	0.250	2.36
$NaNO_3$	0.125	3.33
HNO_3	0.100	3.07
HNO_3	0.010	8.44

No specific relationship is obtained by plotting μ or $\sqrt{\mu}$ against k or log k. It appears from Table III that K^+, Mg^{2+} and NH_4^+ as also SO_4^{2-} have inhibiting action on this reaction. Table IV records the constants in presence of nitrates.

Nitrate is found to inhibit the reaction to a great extent. The same behaviour was noted by Gupta and Ghosh (*loc.cit.*) in the silver-catalysed oxidation of oxalate. On the other hand, in the oxidation of arsenious acid, both catalysed and uncatalysed (*loc.cit.*), it is reported to be a good catalysing ion. This difference in behaviour must be accounted for by different reaction mechanisms of these oxidations. However, it is clear from Tables III and IV that K^+, Na^+ and NH_4^+ have less inhibiting action than the nitrate ion.

Reaction in presence of Sodium Acetate.—Table V records the rate constants at different concentrations of sodium acetate and acetic acid. It has an irregular behaviour as in the oxidation of arsenious acid (*loc. cit.*). It appears that acetate ion accelerates, and sodium ion and undissociated molecule of sodium acetate retard the rate, and that the combined effect of these makes the reaction very complicated. Kinetics were followed also in absence of sulphuric acid to ascertain the exact nature of the effect of sodium acetate. The only conclusion drawn is that the acetate ion has a catalytic activity. The results in absence of sulphuric acid were irregular and varied within wide limits.

TABLE V

Conditions are the same as in Table III.

	Sodium acetate.					Acetic acid.	
Conc. (*M*) ..	0.25	0.125	0.05	0.01	0 005	0 10	0.01
k	6.12	12.00	18.72	12.53	21.59	13.92	16.57

Frequency Factor.—Investigations were also made at 40 and 45° to determine the energy of activation and then to calculate the frequency factor (Table VI).

TABLE VI

Conditions are the same as in Table III.

	At 40°.		At 45°.	
Time.	$Na_2S_2O_3$.	*k*.	$Na_2S_2O_3$.	*k*.
0 min.	5.00 c.c.	...	5.00 c.c.	...
10	4.06	20.83	3.74	29.04
20	3.52	17.56	2.76	29.71
30	2 94	17.71	2.04	29 92
40	2.46	17.74	1.52	29 78
50	2.08	17.55	1.20	29.21
60	1.72	17.78	0.98	27 14
70	1.44	17.78	0 80	26.21
80	1.22	17.64	...	...
90	1.02	17.67	...	...

The energy of activation and the frequency factor were found to be $\simeq$ 20900 cal. and $\simeq 1.28 \times 10^{11}$ litres/mole/sec. respectively. The rate constants slightly decrease at 45°, probably due to slight decomposition of persulphate, liberating oxygen at this temperature, and for this reason the last few observations were ignored for calculating the average. The frequency factor must be considered only qualitative, but its order of magnitude does help one to arrive at a possible reaction mechanism. This frequency factor corresponds to the overall reaction, and it may be different for the rate-determining step.

Mechanism

The reaction is first order in persulphate and independent of the concentration of formic acid. Hence, the rate-determining step does not involve the reductant concentration as in other persulphate reactions. Salt-effect could not be determined owing to the specific influence of ions. The following mechanism is proposed for this reaction.

$$S_2O_8^{2-} \rightleftharpoons 2\,SO_4^- \qquad \text{rapid (I)}$$

$$2\,SO_4^- + Ag^+ \rightarrow 2SO_4^{2-} + Ag^{3+} \qquad \text{slow (II)}$$

$$HCOO^- + Ag^{3+} \rightarrow H^+ + CO_2 + Ag^+ \qquad \text{fast (III)}$$

The existence of free radicals, SO_4^- and OH, and of higher valent silver, Ag^{3+}, is now beyond doubt (Uri, *Chem. Rev.*, 1952, **50**, 375). Gupta and Ghosh (*loc. cit.*) and Yost (*J. Amer. Chem. Soc.*, 1926, **48**, 152) have already discussed the possibility of higher valent silver in other silver-catalysed oxidations by persulphate. A comparison of the observed frequency factor with the normal value 1×10^{11} does not support the generally accepted mechanism :

$$S_2O_8^{2-} + Ag^+ \longrightarrow 2SO_4^{2-} + Ag^{3+}.$$

If this were the rate-determining step, the observed frequency factor should have been much higher than 1×10^{11}, the reaction being between oppositely charged ions (Frost and Pearson, "Kinetics and Mechanism", Wiley, New York, 1953, p. 132). Our slow step of reaction is also between oppositely charged ions, and it has a greater value of frequency factor than the normal, because this step is preceded by an equilibrium which has a very small K, of the order of 10^{-8} or even less. The slow step (II) has a first order dependence on persulphate and has a higher value of frequency factor, as shown below.

$$-dc/dt = k_2\,[Ag^+]\,[SO_4^-]^2$$

but $$K\,[S_2O_8^{2-}] = [SO_4^-]^2 \qquad \text{from (I)}$$

Hence $$-dc/dt = k_2 . K\,[S_2O_8^{2-}]\,[Ag^+]$$

$$= k_r\,[S_2O_8^{2-}]$$

where $$k_r = k_2 . K\,[Ag^+]$$

Silver-ion concentration remains constant and the slow step is thus of first order in persulphate. Experimentally determined rate constant, k, is equal to $k_r/[Ag^+]$. Hence, $k = k_2 . K$ or $k_2 = k/K = 10.20/10^{-8} = 10.20 \times 10^8$ litres/mole/min.

Based on this value of k_2, the frequency factor for the step (II) is $\simeq 1.28 \times 10^{19}$ litres/mole/sec. We thus come to the conclusion that the slow step is more likely between oppositely charged ions than between persulphate and silver ions; it is between positive silver ion and a negative radical ion obtained from persulphate.

Step (II) of the mechanism is ordinarily quite fast. When, however, the concentration of formic acid is low, this step is not as fast, and some of Ag^{3+} ions react with water, producing OH, which probably does not oxidise formic acid or does so only slowly.

$$Ag^{3+} + 2H_2O = Ag^{+} + 2H^{+} + 2OH.$$

OH liberates iodine from potassium iodide in the iodometric analysis, thus providing higher estimated values of persulphate and decreasing velocity constants. The same behaviour was noted in the oxidation of oxalate by Gupta and Ghosh (*loc.cit.*). In fact, oxidation of oxalate and formic acid are similar in many respects. Mention has already been made of the specific influence of the ions in these two oxidations. In this connection it may be stated that the silver-catalysed oxidations of oxalate, arsenious acid and formic acid have the same order of magnitude of velocity constants, and, hence, they belong to one type as distinct from the other type of catalysed oxidations, such as those of Cr^{3+} (Yost, *loc.cit.*), VO^{2+} (Yost and Claussen, *J. Amer. Chem. Soc.*, 1931, **53**, 3349), Mn^{2+} (Dekker *et al.*, *ibid.*, 1937, **59**, 2129), Ce^{2+} (Cone, *ibid.*, 1945, **67**, 78) etc. Table VII records the rate constants for these ions.

TABLE VII

Reductant	k. (litres/mole/min.)	Temp.	Electrolyte present other than reactants.		Reference.
K-oxalate	18.58	30°	0.09 M	H_2SO_4	Gupta & Ghosh
H_3AsO_3	18.80	24°	0.10	,,	Gupta & Misra
H_3AsO_3	30.54	29°	...	...	Gupta & Misra
HCOOH	10 20	35°	0.10	,,	...
HCOONa	11 96	35°	0.10	,,	...
Mn (II)	0.45	35°	0 25	K_2SO_4	Gupta & Ghosh
Mn (II)	0.25–0 30	25°	0 10	HNO_3	Dekker *et al.*
Cr (III)	0.30–0.33	25°	0 09	H_2SO_4	Yost
VO(II)	0.30–0.36	25°	0.10	$HClO_4$	Yost & Claussen
Ce(II)	0.40–0 45	25°	...	...	Cone
N_2H_4	0 40–0.50	25°	0.09	,,	Dekker *et al.*

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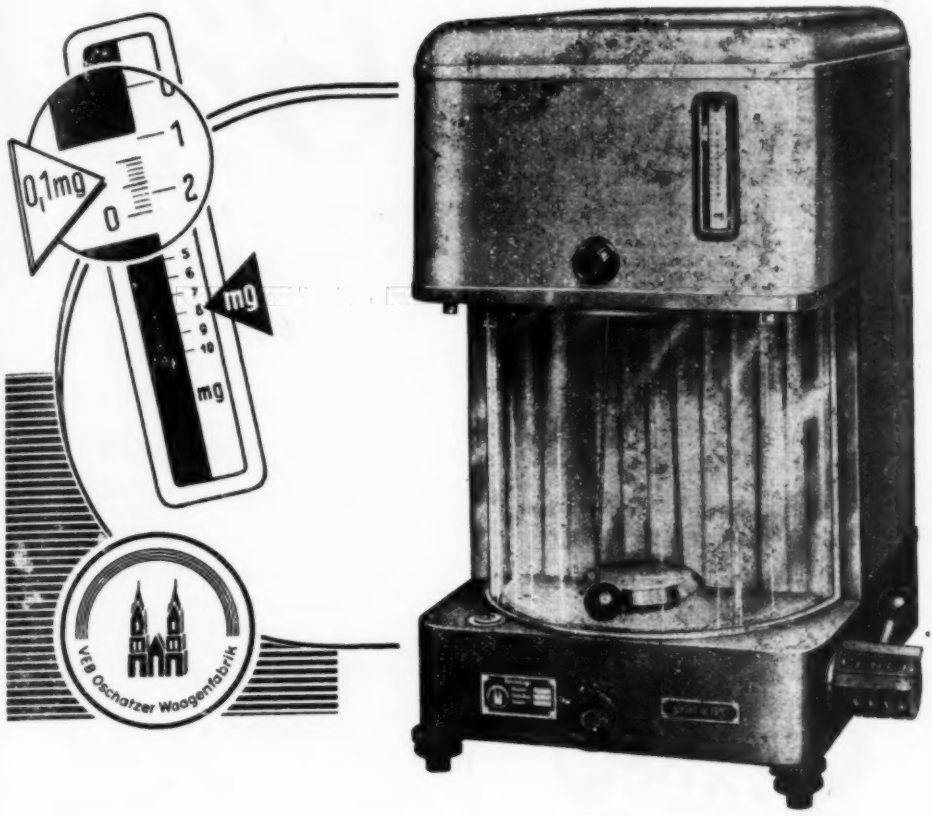

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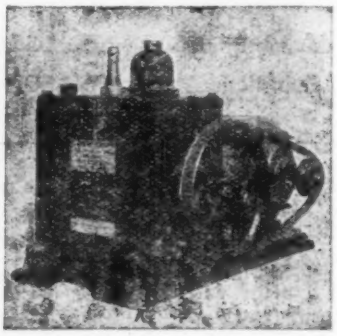

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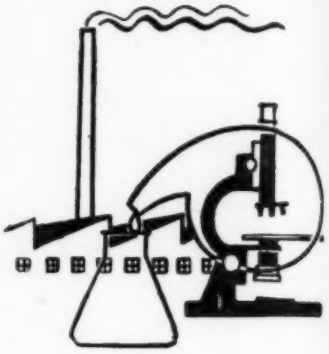

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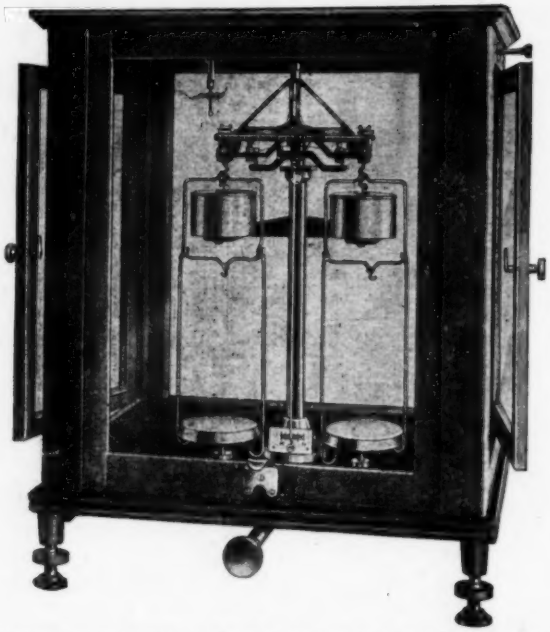

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